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Field Intercomparison of Precipitation Samplers for Assessing Wet Deposition of Organic Contaminants

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16. ABSTRACT

A field intercomparison of four wet-only precipitation samplers were performed to assess their ability to efficiently collect rain and selected organic contaminants. Samplers are evaluated and compared on the basis of their ability to efficiently collect rainfall, exhibit mechanical reliability, demonstrate adequate operational characteristics and provide precise measures of wet-only inputs. The most significant difference between the four samplers was their mechanical reliability in the field. The samplers performed equally well in assessing organic concentrations in rain.

This sampler intercomparison was conducted in part to select the preferred characteristics of a rain sampler that must be deployed in the field unattended for up to two weeks. The MIC sampler, properly maintained, is suitable for such a purpose. Of the two modes of compound isolation tested, the resin adsorbent (XAD-2) exhibited modestly higher concentrations that the solvent MIC but had the disadvantage of ease of sample handling and lower blanks. Both could be operated with proper maintance to provide precise data. The stainless steel and Teflon coated funnel surfaces pro vided comparable data.

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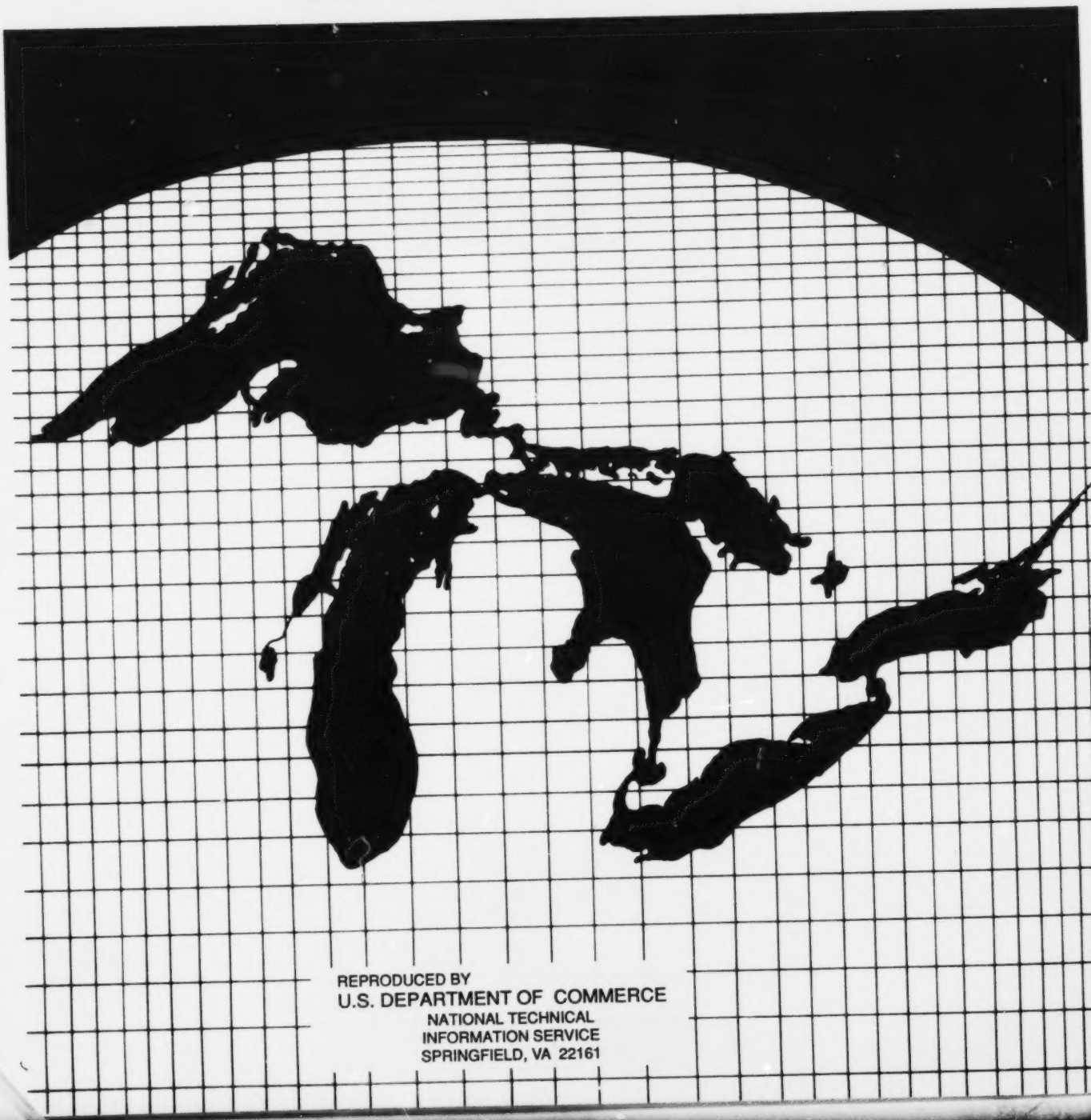

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FIELD INTERCOMPARISON OF PRECIPITATION SAMPLERS FOR ASSESSING WET DEPOSITION OF ORGANIC CONTAMINANTS

by

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OUTLINE

Summary 1

Introduction 4

- Statement of the Problem
- Objectives
- Strategy

Processes of Wet Deposition 6

Experimental Section 11

- Site Description
- Sampler Design
- Sampling Protocol
- Analytical Protocol
- Quality Assurance/Quality Control

Results and Discussion 39

- Criterea for Precipitation Collectors
- Rain Collection Efficiency
- Organic Contaminant Collection Efficiency
- Sampling Protocol Affecting Collection Efficiency
- Mechanical Reliability and Operational Characteristics

Conclusions 82

Acknowledgements 85

References 86

LIST OF TABLES

1. Operational Variables of Precipitation Samplers
2. Selective Ion Monitoring Program for PAH on GC-MSD
3. Chromatographic Conditions for Analysis of PAHs and Chlorinated Hydrocarbons
4. PCB Congener Numbers and Structures
5. Organic Compounds Analyzed in Wet-Only Precipitation
6. Summary of Analytical Quality Control Data
7. Recovery of Procedural Surrogates
8. Rain Sampler Collection Efficiency
9. Volume-Weighted Mean Concentrations for Fourteen Organic Compounds in Wet-Only Precipitation - 1986
10. ANOVA Comparison of Fourteen Compounds in Four Precipitation Samplers
11. Percentage of Compound Mass in Funnel Rinse
12. Percentage of Total Compound Mass on the Filter (FM Sampler)
13. Problems in Field Operation

SUMMARY

The atmosphere is recognized as an important contributor of organic contaminants to oceanic and lacustrine environments. In the case of the Laurentian Great Lakes, it has been estimated that atmospheric deposition represents an important if not dominant fraction of total inputs of many chemicals from all sources. Atmospheric deposition results from wet and dry inputs. The objectives of this project were to perform a field intercomparison of four wet-only precipitation samplers in an assessment of their ability to efficiently collect rain and selected organic contaminants. The samplers are evaluated and compared on the basis of their ability to efficiently collect rainfall, exhibit mechanical reliability, demonstrate adequate operational characteristics and provide precise measures of wet-only inputs. The samplers differed in collection surface area (0.08 to 0.21 m^2), type of collection surface (stainless steel; Teflon coated), mode of organic compound isolation (resin adsorbent; batch extraction) and operational characteristics. We found that the most significant difference between the four samplers was their mechanical reliability in the field. The samplers performed equally well in assessing organic concentrations in rain.

The four samplers were deployed in May 1986 at a site about 50 km northwest of the Twin Cities. During the 1986 field season, wet-only precipitation samplers collected rainfall integrated over periods of 5

to 20 days (average = 14 days). Samples were analyzed for approximately 60 organic contaminants including polycyclic aromatic hydrocarbons (PAHs) and chlorinated hydrocarbons including polychlorinated biphenyls (PCBs), chlorinated pesticides and chlorinated benzenes. Fourteen of these compounds selected on the basis of differing physical-chemical properties and occurrence in rainfall were used as the basis of the intercomparison.

The four rain samplers captured from 82 to 90% of the rain gauge precipitation. When periods of sampler malfunctioning were removed, all samplers collected at ≈ 95% efficiency. Problems encountered varied from blown fuses and loose bolts on the movable arm to vandalism. The key to proper collection of precipitation is to monitor and properly maintain all samplers.

Volume-weighted mean (VWM) concentrations of the fourteen compounds and propagated errors for each were calculated. The simple criterion applied to the question of whether the samplers behaved differently was whether the error bars overlapped for individual compounds observed for different samplers. With few exceptions, there was little or no significant difference between the four samplers based on VWMs. For all compounds, the samplers containing adsorbent resins provided an average 5 to 10% higher VWM concentration than observed for the sampler using batch extraction. A one-way ANOVA comparison of the 14 compounds was conducted to test the null hypothesis that there is no difference between sampler behavior based on event-to-event variations. With few exceptions, these data support the null hypothesis that there is no or little significant difference

in the collection efficiency of these 14 compounds. Where differences were significant, no consistent pattern emerged.

One characteristic exhibited by all compounds and all samplers is the retention of organic contaminants on the collection surface and/or sampling train. For example, an average of 26% of the PAH and 40% of the $\sum$ PCB mass in the sample occurred in the solvent rinse of the funnel and sampler train. Although not a problem in assessing total concentrations, this phenomenon makes the determination of speciation in rain samples and of atmospheric removal processes all but impossible. Collection of total compound mass requires the rinsing of funnel surfaces with solvent and analyzing the rinse with the sample.

The intercomparison of wet-only, integrating rain samplers was conducted in part to select the preferred characteristics of a rain sampler that must be deployed in the field unattended for up to two weeks. The MIC sampler, properly maintained, is suitable for such a purpose. Of the two modes of compound isolation tested, the resin adsorbent (XAD-2) exhibited modestly higher concentrations than the solvent MIC but had the disadvantage of higher blanks and clogging. Alternatively, the solvent MIC sampler had the advantage of ease of sample handling and lower blanks. Both could be operated with proper maintenance to provide precise data. The stainless steel and Teflon coated funnel surfaces provided comparable data.

Three of the rain samplers had equal collection surface areas of 0.21 m^2. Side-by-side operation permitted comparison of sampler variability. These data suggest that the expected uncertainty in loading estimates of organic contaminants at trace concentrations may be no better than $\approx$ 20%.

INTRODUCTION

The atmosphere is now recognized as an important contributor of anthropogenic organic compounds to oceanic (Bidleman and Olney, 1974; Atlas and Giam, 1981, 1985; Tanabe et al., 1983) and to freshwater ecosystems (Murphy and Rzeszutko, 1977; Andren, 1983; Murphy, 1984; Eisenreich et al., 1981; Strachan and Huneault, 1979; Strachan, 1984). The Laurentian Great Lakes are recognized as being particularly susceptible to atmospheric inputs of organic contaminants because they are near and generally downwind of major/industrial centers, have large surface area to basin area ratios and have long water residence times (Eisenreich et al., 1981). Estimates of wet and dry deposition, especially for contaminants such as polychorinated biphenyls (PCBs) using input-output budgets show that the upper lakes (Superior, Michigan, Huron) receive the majority of total inputs from the atmosphere (Strachan and Eisenreich, 1987). The lower lakes (Erie, Ontario) receive a lower but significant percentage of their total input from atmospheric deposition. The organic contaminants are removed from the atmosphere and deposited on water by wet deposition (rain, snow), dry particle deposition and vapor absorption at the air-water interface. The latter two constituting dry deposition are at best difficult to infer from environmental measurements and models (Doskey and Andren, 1981; Slinn et al., 1978; Mackay et al., 1986). However, precipitation inputs may be properly assessed using wet-only integrating or event samplers of various designs (e.g., see Strachan

and Huneault, 1984; Pankow et al., 1984) employing either in-situ compound isolation or bulk water extraction. The Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency (EPA) seeks to modify its existing atmospheric monitoring network to include measurement of atmospheric inputs of organic contaminants (Eisenreich, 1986; Murphy, 1987). To that end, the objective of this study was to intercompare four precipitation samplers co-located at a site 50 km north-northwest of Minneapolis, Minnesota. It is anticipated that precipitation samplers will be deployed in the modified network for periods up to two weeks and must be capable of unattended operation. The samplers are evaluated and compared on the basis of their ability to efficiently collect rainfall, exhibit mechanical reliability, demonstrate good operational characteristics and provide precise measures of wet-only inputs of selected organic contaminants. The samplers differed in collection surface area (0.08 to 0.21 m^2), type of collection surface (stainless-steel; Teflon-coated), mode of compound isolation (resin adsorbent; batch extraction) and other operational characteristics. Fourteen compounds were selected out of about 60 compounds analyzed to determine the difference in sampler behavior. The atmospheric processes governing wet deposition can influence collection results and will be described here.

Processes Governing Wet Deposition

The mechanisms of chemical removal from the atmosphere are very different for particle associated compounds than for gas phase compounds. The relative importance of these two processes depends on the distribution of the organic compound between vapor and aerosol, particle size distribution and Henry's Law constant (H). Non-reactive organic gases will be scavenged by rain according to H if equilibrium between the gas and aqueous phases is achieved (Slinn et al., 1978; Ligocki et al., 1985). The overall resistance to vapor absorption by rain is a result of resistances in the air phase, in the liquid phase and a surface resistance (Peters, 1983). Assuming surface resistance is negligible, air resistance depends on the relative velocity between the raindrop and air-phase.. The liquid-phase resistance depends on molecular diffusion in the hydrometeor and internal circulation in the droplet. In the absence of chemical reactions in the droplet, an atmospheric gas should attain equilibrium with a falling raindrop in about 10m of fall (Slinn et al., 1978; Scott, 1981; Ligocki et al., 1985). The position of equilibrium defined by H is a function of temperature as it increases by about a factor of two for each 10°C increase in temperature (Ligocki et al., 1985). For PCBs, H increases by a factor of ≈ 4 for each 10°C rise in temperature (Burkhard et al., 1985). Perhaps more importantly, the H values decrease with falling temperatures suggesting temperature-dependent changes in removal efficiency from summer to winter seasons.

The total extent of organic compound scavenging by falling rain may be given as (Ligocki et al., 1985):

$$W_T = Wg\ (1-\phi) + Wp(\phi) \qquad (1)$$

where W_T = overall scavenging efficiency of gases and particles by hydrometeors

$$W_T = \frac{[\text{rain, total}]}{[\text{air, total}]} \qquad (2)$$

Wg is the gas scavenging efficiency

$$Wg = \frac{[\text{rain, diss}]}{[\text{air, gas}]} \qquad (3)$$

Wp is the particle scavenging efficiency

$$Wp = \frac{[\text{rain, particle}]}{[\text{air, particle}]} \qquad (4)$$

and ϕ is the fraction of the total atmospheric concentration occurring in the particle phase.

An atmospheric organic vapor attaining equilibrium with a falling raindrop is scavenged from the atmosphere inversely proportional to H:

$$Wg = \frac{RT}{H} = \alpha \qquad (5)$$

where R is the universal gas constant (atm m^3/mol °K), T is temperature (°K), H = Henry's Law constant (atm m^3/mol), and α = solubility coefficient. Surface flux of a vapor-phase organic compound removed by rain becomes

$$Fg = \alpha \cdot P \cdot Cg = Wg \cdot P \cdot Cg \qquad (6)$$

where P is annual rainfall intensity and Cg is the concentration of organic vapor in the atmosphere, also given by $(1-\phi)C_{AIR,T}$. Field determined W_T values are often substantially larger than Wg values based on H for many organic compounds having $P_V \leq \approx 10^{-5}$ torr suggesting particle scavenging by precipitation is an important flux term. Slinn et al., (1978), Scott (1981), Eisenreich et al., (1981), Bidleman and Foreman (1987), Peters (1983) and Atlas and Giam (1985) present estimated Wg values. Ligocki et al., (1985) have recently reported gas scavenging efficiencies for a variety of nonpolar organic compounds measured in the field in Portland, OR. They compared field-determined Wg values to those estimated from consideration of H and ambient temperatures. Wg values ranged from 3 to 10^5 (dimensionless) for tetrachloroethylene and dibutylphthalate, respectively. Field Wg values (Wg) were calculated as:

$$\bar{W}g = (10^3 L/m^3) \frac{[\text{rain, dissolved}]\ (ng/L)}{[\text{air, gas}]\ (ng/m^3)} \qquad (7)$$

These values for Wg were underestimated by factors of 3 to 6 using H data at 25°C applying the relationship provided earlier - $Wg = \alpha = RT/H$. Correcting published H values for ambient temperatures of 5 to 9°C, equilibrium between the atmospheric gas and dissolved constituent in rain was demonstrated for several PAHs and other low MW compounds. Based on these results, temperature-corrected Wg values (estimated from H) may be used to estimate organic vapor concentrations in the atmosphere, temperature-specific H values and/or wet vapor flux if atmospheric vapor concentrations are known.

Precipitation scavenging of particles containing sorbed organic or inorganic species (Wp) permit the calculation of surface fluxes (Ligocki et al., 1985):

$$Fp = Wp \cdot P \cdot Cp = Wp \cdot P \cdot C_T\phi \qquad (8)$$

where Fp is the wet particle flux and Cp is the concentration of atmospheric particulate-bound species. Slinn et al., (1978), Gatz (1975) and Slinn (1983) estimate Wp values for below-cloud scavenging as $\approx 10^3$ to 10^5 for .01 to 1.0 μm particles. Scott (1981) suggests that in-cloud scavenging may produce Wp values on the order of 10^6. Depending on particle size, precipitation intensity, and type of meteorological event, Wp may range from 10^3 to 10^6. The higher value implies that the aerosol is readily incorporated into cloud water and is hygroscopic. The lower value implies a non-hygroscopic, probably carbonaceous particle that is not readily incorporated into cloud water. Aerosol collected over Lake Michigan was about 7 to 50% organic carbon and sub-micrometer in size (Andren and Strand, 1981). Slinn (1983) argues that even carbonaceous particles age into more hygroscopic particles during transport. The relationship of concentration in rain to precipitation intensity also implies whether in-cloud or below-cloud scavenging is operative. In a convective system, the cloud processes air and particles drawn into it. In this way, the concentration of scavenged particles in rain reaching the surface is independent of duration and amount of precipitation (Hicks, 1986). Below-cloud scavenging of particles by rain reduces the number of particles below the cloud, and additional rain dilutes the concentration of previously deposited chemicals in rain.

The most comprehensive study of particle-bound chemical scavenging by precipitation was conducted by Ligocki et al. (1985). They list Wp values of 10^2 to 10^5 for a series of PAHs, alkanes and phthalates. In general, Wp values are consistent with below-cloud and in-cloud scavenging for PAHs, in which the compounds with higher scavenging ratios were associated more frequently with large particles. Particle scavenging ratios for trace metals as reported by Gatz (1975), Talbot and Andren (1983), Settle and Paterson (1982), Slinn (1983), Arimoto and Duce (1987) and others are on the order of 10^4 to 10^6. To adequately predict Wp, detailed information on particle-size distribution, atmospheric concentrations in particle-size ranges and detailed meteorological parameters are needed.

The total wet surface flux (vapor + particle) of organic compounds in the atmosphere may be estimated from:

$$F_{T,W} = W_T \cdot C_{air} = Wg(1-\phi)C_{air} + Wp\phi C_{air} \qquad (9)$$

$$F_T = C_{air}(Wg(1-\phi)) + Wp\phi \qquad (10)$$

$$F_T = \frac{RT}{H}(1-\phi)C_{air} + Wp\phi C_{air} \qquad (11)$$

Total wet atmospheric flux ($F_{T,W}$) is calculated as the sum of vapor and particle contributions. The relative importance of each depends in part on the distribution of the organic compound in the atmosphere between the vapor and particle phases. The research of Junge (1977), Yamasaki et al. (1982), Bidleman and Foreman (1982), and Pankow (1987) provide a theoretical and predictive framework for estimating atmospheric distributions. Research thus far indicates that PCBs, DDT, low molecular weight (MW) hydrocarbons and low MW PAHs exist

primarily in the vapor phase in "clean" or rural airsheds while higher MW PAHs, PCBs and dioxins occur primarily in the particle phase. In "dirty" or urban/industrial airsheds. a greater fraction of the total atmospheric burden for a particular chemical will occur in the particle phase. Wet-only sampling systems must be capable of efficiently collecting both dissolved and particulate species in rainfall to accurately assess total wet flux.

EXPERIMENTAL SECTION

Site Description

The precipitation samplers were deployed at the Cedar Creek Natural History Area (CCNHA) in northern Anoka County, east-central Minnesota (45°25' N, 93°10' W). The Natural History Area (Figure 1) consists of 5460 acres of abandoned agricultural fields, uplands, wetlands and lakes. The site was first under the auspices of the Minnesota Academy of Science and given to the University of Minnesota for use as a field research area.

The precipitation samplers were located on the western edge of the CCNHA in a flat, grass-covered field. The field is flanked by wooded areas to the north, east and south with private land, mostly cultivated fields to the west. The nearest trees are ≈ 40 m northwest of the sampling platform. The approach to the site is from the south by a one lane dirt road. State Highway 65 runs ≈ 1.6 km to the west and Anoka County Highway 24 runs ≈ 0.8 km to the south.

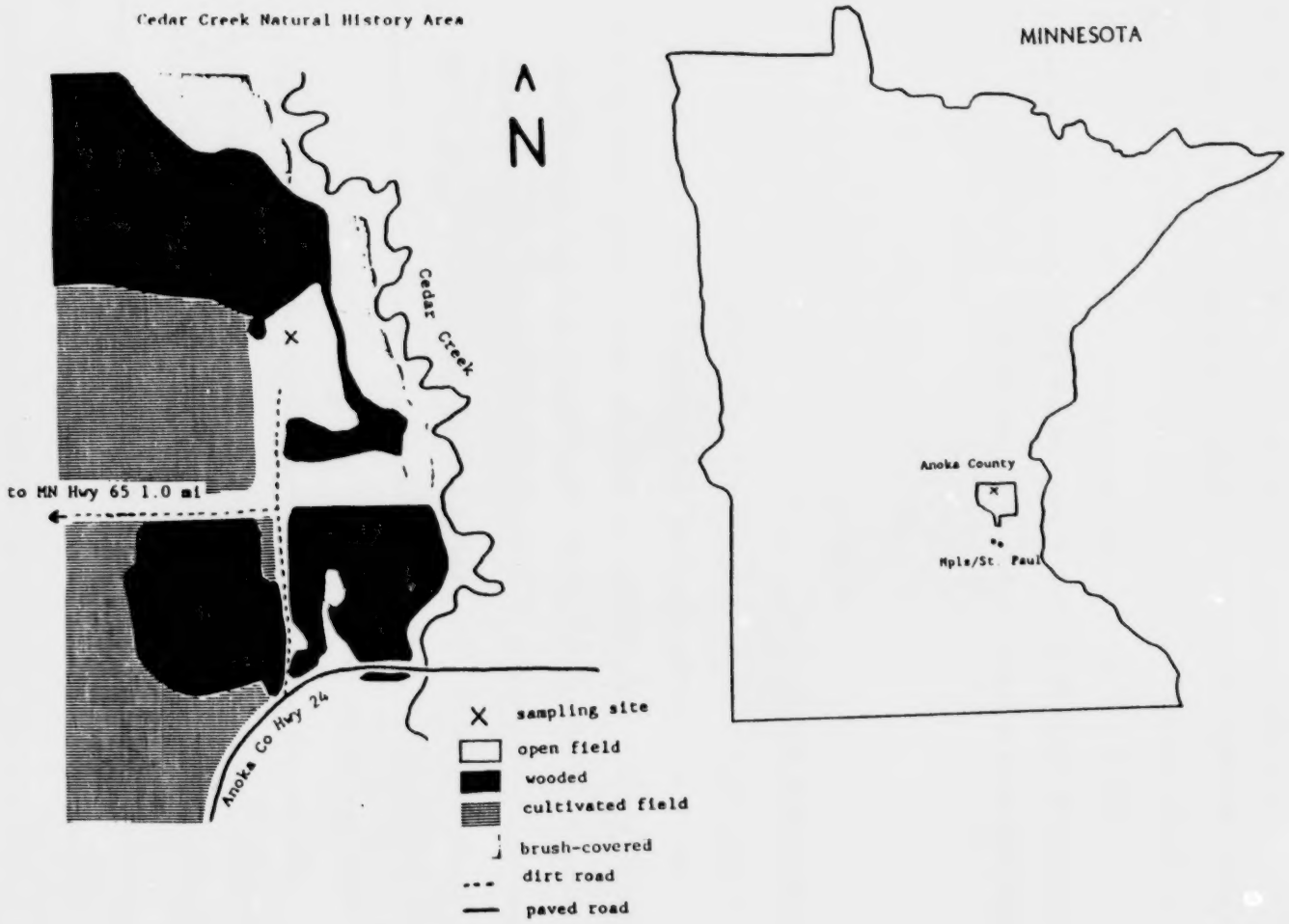


Figure 1. Location of Precipitation Samplers

The samplers were deployed on two Cedar decks about 0.6 m above the ground. They are parallel to the prevailing wind direction (westerly) with the funnels upwind (Figure 2) and are ≈ 2 m apart. All trees or structures in the area subtend at an angle < 15 degrees with the horizon. Two 4-inch rain gauges are located on diagonally-opposite ends of the platform at the same height as the collector funnels.

Sampler Description

All precipitation samplers used in this study are integrating, wet-only precipitation collectors and their characterists are given in Table 1. Three of the precipitation samplers were constructed by M.I.C. Co. (Thornhill, Ontario) and individually modified in their mode of organics isolation, type of collection surface, enclosure of the sample compartment for all-weather adaptation and in-line filtration. Two other samplers constructed by Aerochem Metrics (Bushnell, FL) were also deployed. One was modified for in-situ isolation of organic compounds in rain using XAD-2 resin and the other was used for the collection of inorganic components and organic carbon in rain.

All of the MIC collectors have a square funnel and a cover constructed of stainless steel and have collection surface areas of about 0.21 m^2. The funnel is 0.46 m on a side with a surface slope of 20 degrees toward the center and a 10 cm vertical lip. The legs and chassis are constructed of 0.3 cm cast aluminum. With the cover closed, sampler dimensions are: 1.2 m high x 1.0 m long x 0.5 m wide. A stainless steel screen covers the horizontal surface next to the

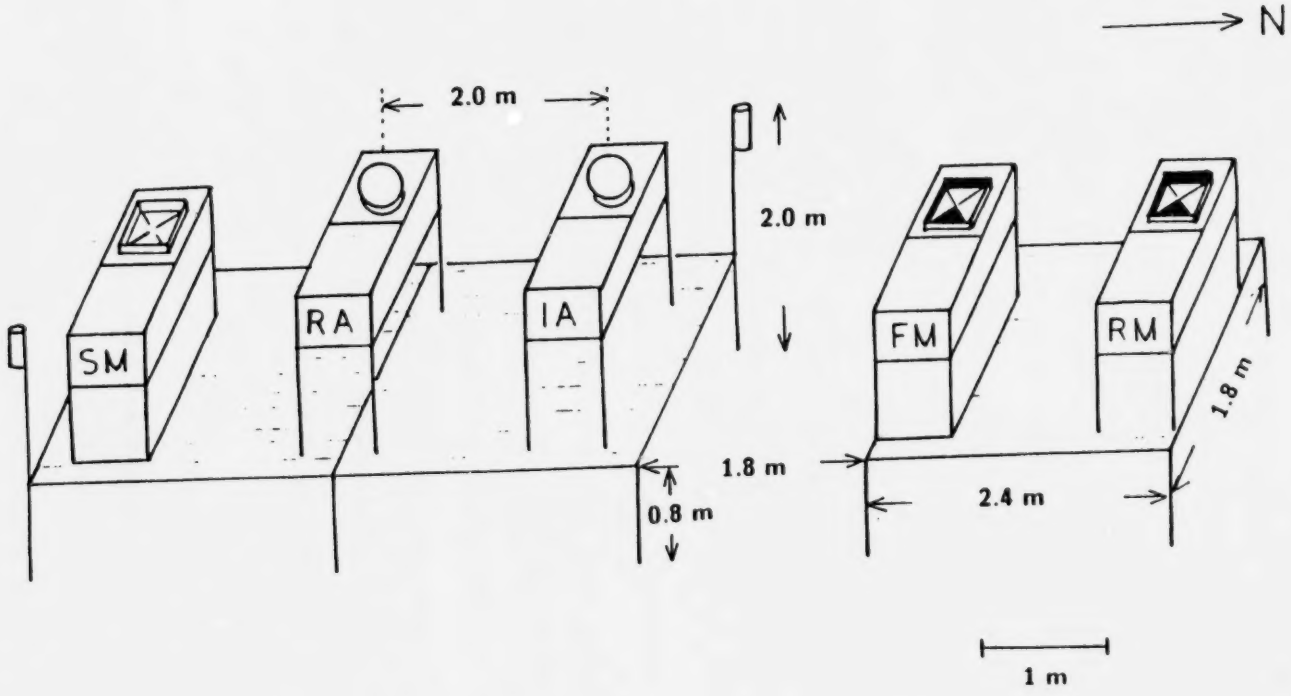


Figure 2. Layout of Precipitation Collectors at Cedar Creek

Table 1

Operational Variables of Precipitation Samplers

Parameter	Solvent MIC (SM)	Resin MIC (RM)	Filter MIC (FM)	Resin Aerochem (RA)
Collection Surface surface area (sq. cm)	2060	2040	2060	814
surface material	stainless steel	teflon	teflon	stainless steel
shape	square	square	square	circular
Collection Efficiency (ave. %) overall	90.4	92.2	88.7	81.6
Mode of Organics Isolation	solvent extraction	XAD-2 resin	XAD-2 resin	XAD-2 resin
Reservior	no	yes	no	yes
Filter	no	no	yes	no
Weather Suitability	all-weather	warm only	warm only	warm only
Collection Capacity	8 L	20 L	20 L	20 L

funnel to reduce rain splash into the funnel. A moisture sensor consisting of two faces at 20 ° from the horizontal is held by an arm slightly above and 0.5 m to the side of the sampler. The sensor controls the automated opening and closing of the cover and is driven by a 1/50 hp gear-motor. The electronics and motor are enclosed in the compartment next to the funnel. The basic MIC sampler has been described in detail by Strachan and Huneault (1984).

One MIC sampler was modified by Chan and Perkins (1986) to include compound isolation by solvent extraction (SM sampler) in the following manner. Organic compounds are isolated <u>in-situ</u> by passive solvent extraction rather than resin adsorption (Figure 3). The lower part of the sampler is enclosed, insulated with 1/2 inch styrofoam and warmed by two thermostatically-controlled heaters during cold-weather sampling. This sampler has a stainless steel funnel surface with heating cable attached to the underside of the funnel. Precipitation flows from the funnel through 1/4 inch Teflon tubing into a four litre solvent bottle. A short section of the tubing leading to the bottle is flexible and can be closed by a pinch clamp controlled by a solenoid valve; this isolates the sample from the atmosphere during dry periods. The tubing extends to the bottom of the bottle where there is a 200 mL layer of dichloromethane (DCM) of 3-4 cm thickness. The water must first pass through the DCM layer which is more dense and remains on the bottom as the bottle fills. This serves as the initial extraction step. Teflon tubing leads to a second bottle which collects the overflow. Another solenoid valve controls venting and flow between the two bottles. The total collection capacity is 8 L.

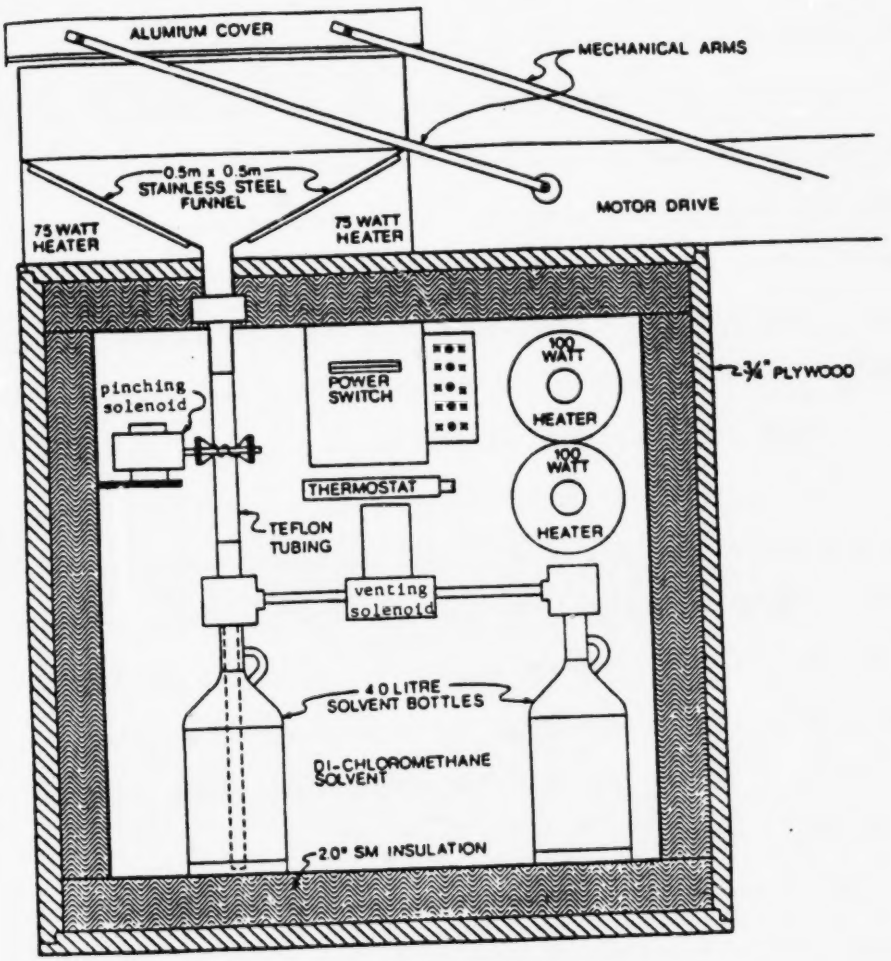


Figure 3. Schematic of Solvent MIC Sampler (SM)
(Chan and Perkins, 1986)

When exceeded, water spills out of the second 4-L bottle through a hole in the cap and the actual volume of precipitation collected is unknown. The SM sampler was on loan to this project by C.H. Chan of the National Water Research Institute, Burlington, Ontario.

The resin MIC sampler (RM) has a Teflon-coated funnel surface having a collection area of 0.21 m^2 (Figure 4). A two-litre glass reservoir covered with aluminum foil is located directly below the funnel. This is followed by a Teflon cartridge containing XAD-2 resin. The cartridge is made of 0.5 cm thick Teflon pipe, 15 cm long with an inside diameter of 1.5 cm (Figure 5). The tubing is connected by stainless-steel Swagelok fittings on either end. Glass wool plugs on each end hold the resin in place. Water flows from the funnel into the reservoir; since the flow through the resin cartridge averages about 40 mL/min under gravity, the reservoir holds the sample to ensure that it is not exposed to open air or direct sunlight before extraction by the resin. After the water flows through the resin cartridge, it drains into a 20-L plastic carboy where it is held for volume measurement.

The Filter MIC sampler (FM) also has a Teflon-coated funnel surface and has a collection area of 0.21 m^2. The space below the funnel is enclosed but not insulated or heated. The FM sampler is similar in operation to the RM collector except there is an in-line filter installed just above the resin cartridge. The type of filter used was a 47 mm Gelman AE glass fibre filter held in a Nacom Teflon filter assembly. The FM sampler was on-loan to this project by Maris Lucis of the Ontario Ministry of the Environment, Toronto.

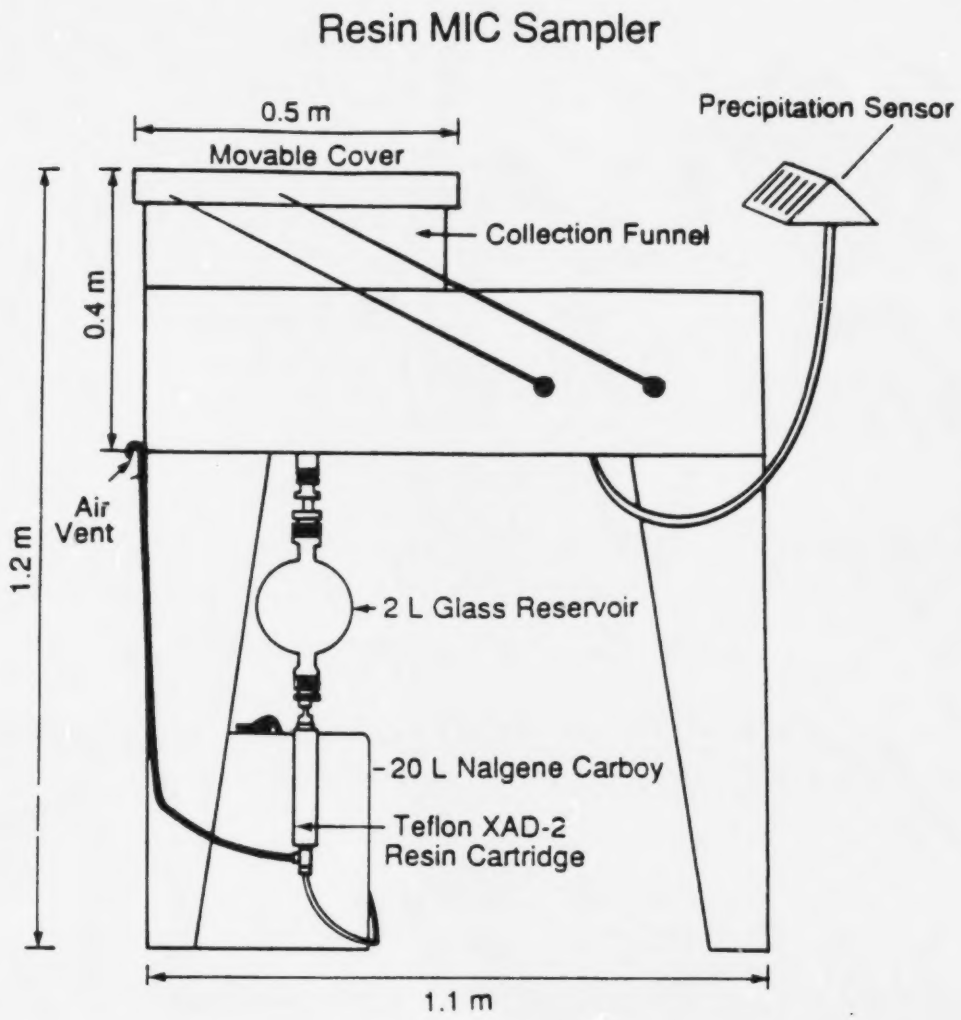


Figure 4. Schematic of Resin MIC Sampler (RM)
(Strachan and Huneault, 1984)

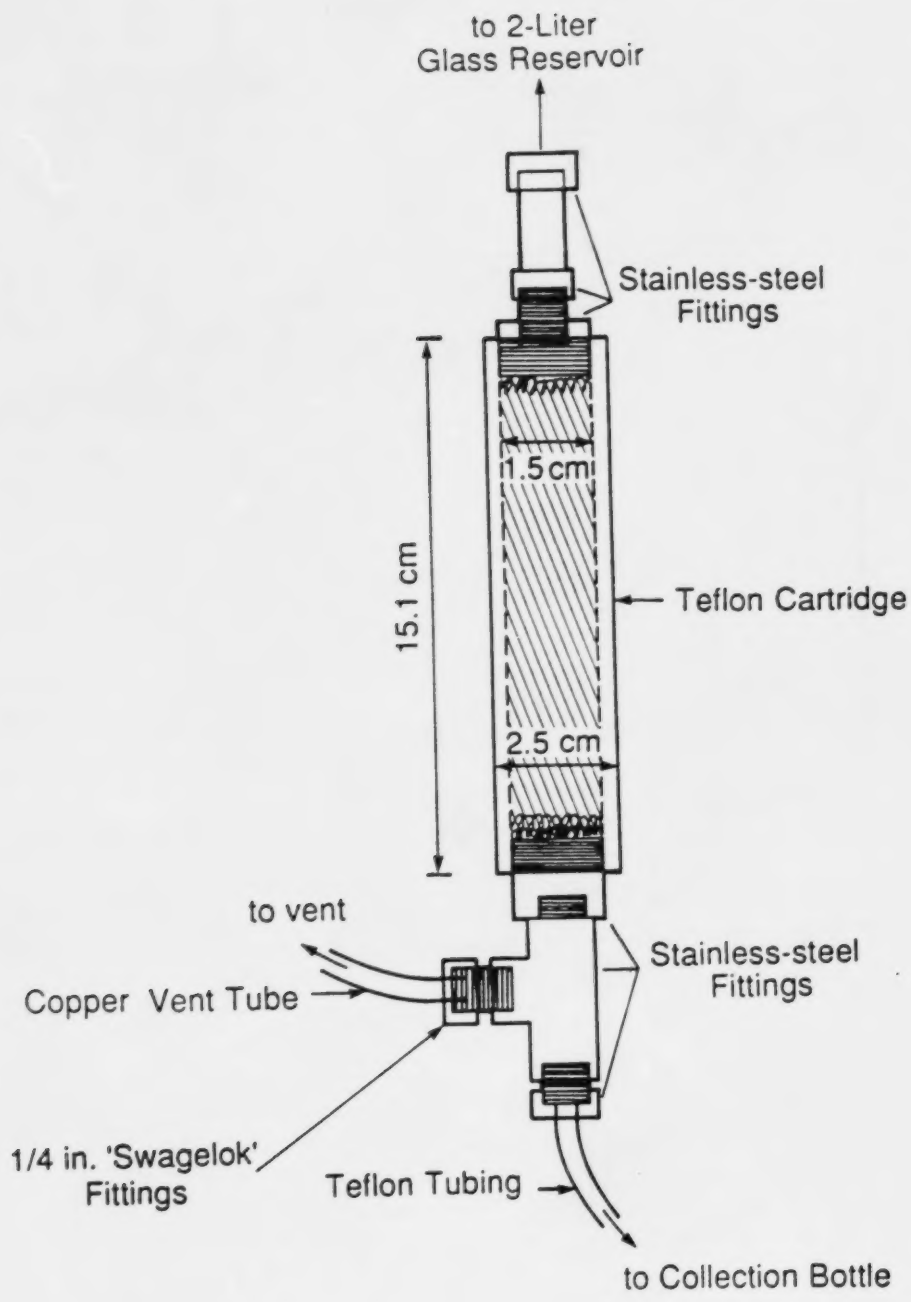


Figure 5. Schematic of XAD-2 Resin Adsorbent Cartridge

The Aerochem Metrics sampler (RA) is an automated wet-only precipitation collector constructed of 0.4 cm thick aluminum. The electric motor and mechanism for operating the cover are located underneath the collection surface. Overall dimensions are: 1.3 m high to the top of the bucket or funnel, 0.4 m wide and 0.9 m long. The moisture sensors have one face and are held closer to the body of the collector than for the MIC samplers. The Aerochem Metrics sampler was modified for in-situ organics isolation by resin extraction (similar to Figure 4). A round stainless-steel funnel of 0.08 m^2 surface area was installed in place of the normal plastic bucket. The area below the funnel is not enclosed. Collection and isolation are similar to operation of the RM sampler. The other Aerochem Metrics sampler was operated with a plastic bucket to collect precipitation for inorganic ion and organic carbon analyses.

Sampling Protocol

Precipitation was collected in periods ranging from 5 to 30 days depending on the amount of rainfall at the site (average = 14 days). All of the sampling materials such as solvents, sample bottles, resin cartridges and tools were transported to the site in a large, covered polycarbonate tote box.

At the sampling site, the amount of precipitation collected by the twin 4 inch rain gauges was measured and recorded to the nearest 0.01 inch. The rain samplers were then checked for standing water in the funnels or reservoirs; if all water had not passed through the resin cartridge, a peristaltic pump was installed in-line and the standing water pumped through the cartridge and into the 20-L carboys.

The SM sampler was checked for overflow; if the second bottle was completely full, it was noted that sample overflow may have occurred and an accurate measure of the sample volume was not possible.

The volume of water collected in the carboys attached to the resin samplers was measured with a 2 L graduated cylinder, and the water discarded after measuring. The volume collected in the SM sampler bottles and inorganic bucket was measured later in the laboratory.

The procedure for replacing the resin cartridge was similar for all three resin samplers. The cartridge was disconnected, capped, labeled and wrapped in aluminum foil. Then the funnel surface was rinsed with 200 mL of solvent (either acetone or methanol) which was collected in 250 mL amber glass bottles at the point where the cartridge connects to the sampler. The sampler was flushed with 250 mL of Milli-Q water (not collected) and the replacement cartridge installed. The resin was wetted by pouring 250 mL Milli-Q water into the sampler funnel.

The SM sampler bottles were changed in a similar manner; the 4 L amber glass bottles were disconnected and capped, and the funnel was rinsed with solvent. Then the sampler was flushed with Milli-Q water, the replacement bottles attached and the system wetted with 250 mL of Milli-Q water.

The inorganic sampler required only replacing the sample bucket with a clean, empty bucket and covering the first bucket with a tight-fitting plastic lid. All of the samples (i.e., resin cartridges, SM bottles, rinse bottles, inorganic species bucket) were labeled with

sampler ID and date of removal from the sampler.

The motor drive for each MIC sampler was checked for proper operation and loose connections; frequently the allen bolt holding the drive chain sprocket to the motor shaft required tightening. Finally, the moisture sensors for all samplers were activated to ensure correct operation of the covers.

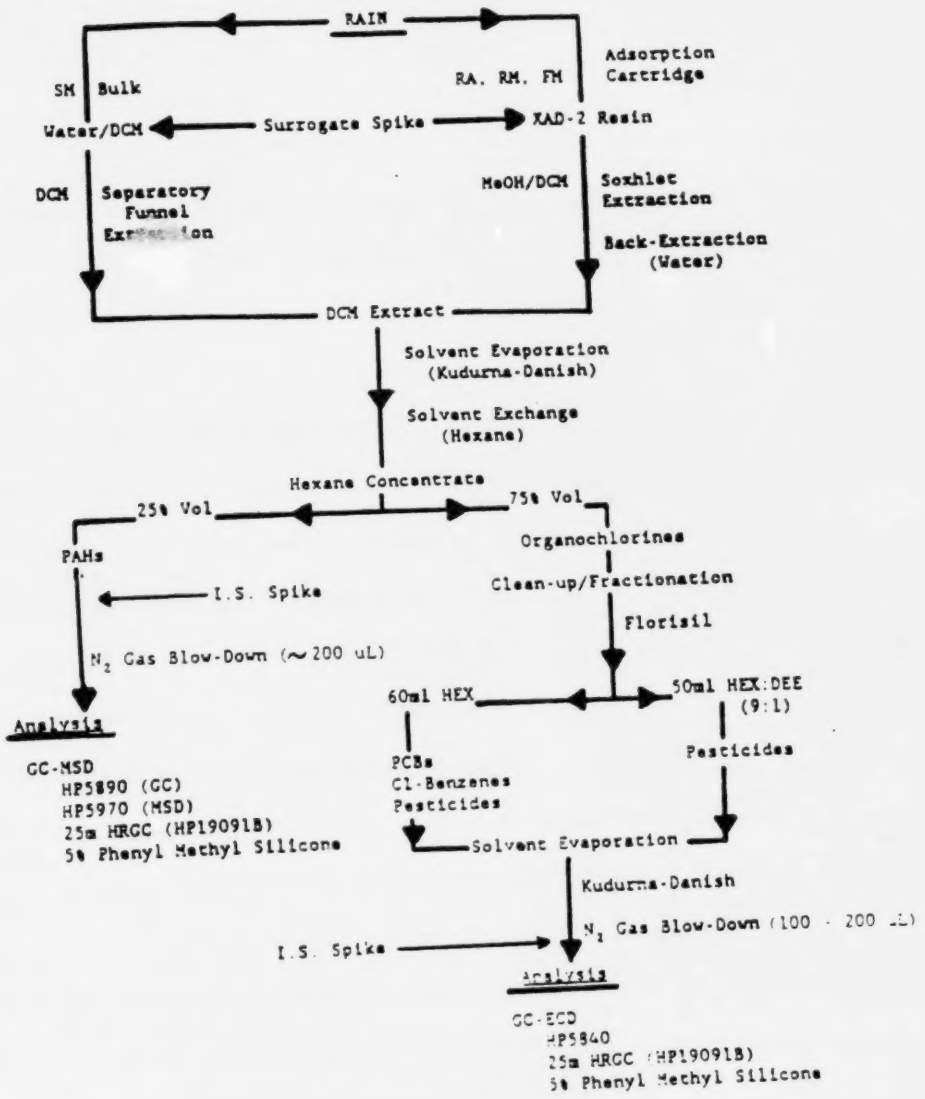
Analytical Procedure

All materials were thoroughly cleaned before use to avoid contamination. The glassware was washed with soap and water, rinsed with solvents and dried to 110 °C. Pesticide grade solvents (Omnisolve, EM Science; High Purity Solvent, American Burdick and Jackson) and cleaned XAD-2 resin gave low blanks which did not interfere with analyte identification or quantification. The XAD-2 resin was cleaned in sequential 48 hour extractions using the solvent series: methanol, acetone, hexane, petroleum ether, acetone, methanol and then rinsed with and stored in Milli-Q water. Care was taken to reproduce this procedure exactly as XAD-2 resin is known to present difficulties in the analysis of chlorinated hydrocarbons by electron capture gas chromatography. Florisil (60-100 mesh) was extracted for 24 hours in a Soxhlet apparatus with 1:1 (v/v) hexane/acetone, activated at 550-600 °C overnight and stored at 110°C.

The overall analytical scheme shown in Figure 6 describes the general procedures by which the polyaromatic hydrocarbons (PAHs) and chlorinated hydrocarbons (CHs) in precipitation samples were analyzed. The bulk rain samples containing DCM from the SM sampler and the XAD-2 resin from the RM, FM and RA samplers were spiked with surrogate

FIGURE 6.

Schematic of Analytical Procedure for the Analysis of PAHs, PCBs, Cl-Pesticides, and Cl-Benzenes.



standards 1,4 dibromobenzene, mirex and d-10 anthracene to obtain analytical recoveries. The SM water samples were extracted in a 5 L separatory funnel with 400 mL additional DCM while the resin samples were sequentially extracted for 24 hours with 1:1 methanol/DCM in a Soxhlet apparatus. The methanol was then removed from the extracts by back extraction with Milli-Q water. The field rinses of the sampler surfaces were either analyzed separately (early in the project) or incorporated into the rain extract. The resulting DCM extracts were dried over anhydrous Na_2SO_4 and concentrated to about 10 ml in a Kurdurna-Danish apparatus with a concomitant solvent change to hexane. The hexane extract was sub-sampled for PAH analysis removing about 25 % of the volume. The remaining extract containing the CHs for analysis was fractionated on a 1.25 % (w/w) water-deactivated Florisil column (13g; 2 cm i.d.) to remove interfering polar compounds and to separate the compounds into a PCB and pesticide fraction. The column was eluted with 60 mL hexane followed by 50 mL of 10 % (v/v) diethyl ether in hexane. These two fractions were concentrated in a Kurduna-Danish apparatus and then blown down under purified N_2 to about 1 mL.

PAHs were quantified in the subsample without further cleanup by isotope dilution gas chromatography - mass spectrometry (GC-MS). The subsample was spiked with an internal standard containing d-8 naphthalene, d-10 phenanthrene, d-12 benzo[a]anthracene, d-12 benzo[a]pyrene and d-12 benzo[ghi]perylene and concentrated to about 100 μL with a gentle stream of purified N_2. The PAHs were analyzed using selective ion monitoring on a HP 5890 GC equipped with a HP 5970 Mass Selective Detector and a HP 59970B computer workstation. The GC-

MSD was operated in the selective ion monitoring mode and scanned for up to seven ions in one of five chromatographic windows (Table 2). Each time window exhibited in Figure 7 and noted in Table 2 contained an internal standard from which response factors were calculated. The run time was about 20 minutes.

The organochlorine fractions were spiked with internal standards 2,3,5,6-tetrachlorobiphenyl and 2,2'3,4,5,6'-hexachlorobiphenyl, and blown down with a gentle stream of N_2 to about 100 μL. The PCBs and other CHs were analyzed on a HP 5840A GC equipped with a ^{63}Ni electron capture detector and a HP 7672A automatic sampler. Chromatographic conditions for the PAHs and CHs are listed in Table 3.

Quantification of all CHs was based on standards of each of the pesticides, PAHs, chlorinated benzenes and PCB congeners. The PCB congeners were represented by those present in standard Aroclor mixtures of 1242, 1254 and 1260. GC-ECD chromatograms of a standard PCB mixture and a rain sample from the SM sampler are shown in Figure 8 detailing the identity of PCB congeners quantified in this study. Table 4 relates IUPAC PCB congener numbers to structure. Capel et al. (1985) list the PCB congener weight fraction in each of the standards. The pesticide standard was a chlorinated pesticide mixture (Supelco) to which hexachlorobenzene (HCB) and mirex were added. The PAH standard was a mixture of 16 priority pollutant PAHs to which benzo[e]pyrene was added (Supelco). Samples 6133-6190 were quantified by externally comparing the area counts of the samples with those of the standards. The chlorinated benzenes in all samples were quantified by comparison to external standards (Ultra Scientific).

Table 2

Selective Ion Monitoring program for PAH on GC/MSD

SIM Group #	SIM Ions	Compound	Quantification Ion
1	127,128,129, 152,153,154 136	Naphthalene	128
		Acenaphthylene	152
		Acenaphthene	154
		D-8 Naphthalene	136
2	165,166,167, 176,178,179, 188	Fluorene	166
		Phenanthrene	178
		Anthracene	"
		D-10 Phenanthrene	188
		D-10 Anthracene	"
3	200,202,203, 226,228,229, 240	Fluoranthene	202
		Pyrene	"
		Benzo[a]anthracene	228
		Chrysene	"
		D-12 Benzo[a]anthracene	240
4	126,250,252, 253,264	Benzo[b]fluoranthene	252
		Benzo[k]fluoranthene	"
		Benzo[e]pyrene	"
		Benzo[a]pyrene	"
		D-12 Benzo[a]pyrene	264
5	138,276,277, 278,279,288	Indeno[1,2,3-cd]pyrene	276
		Benzo[ghi]perylene	"
		Dibenzo[ah]anthracene	278
		D-12 Benzo[ghi]perylene	288

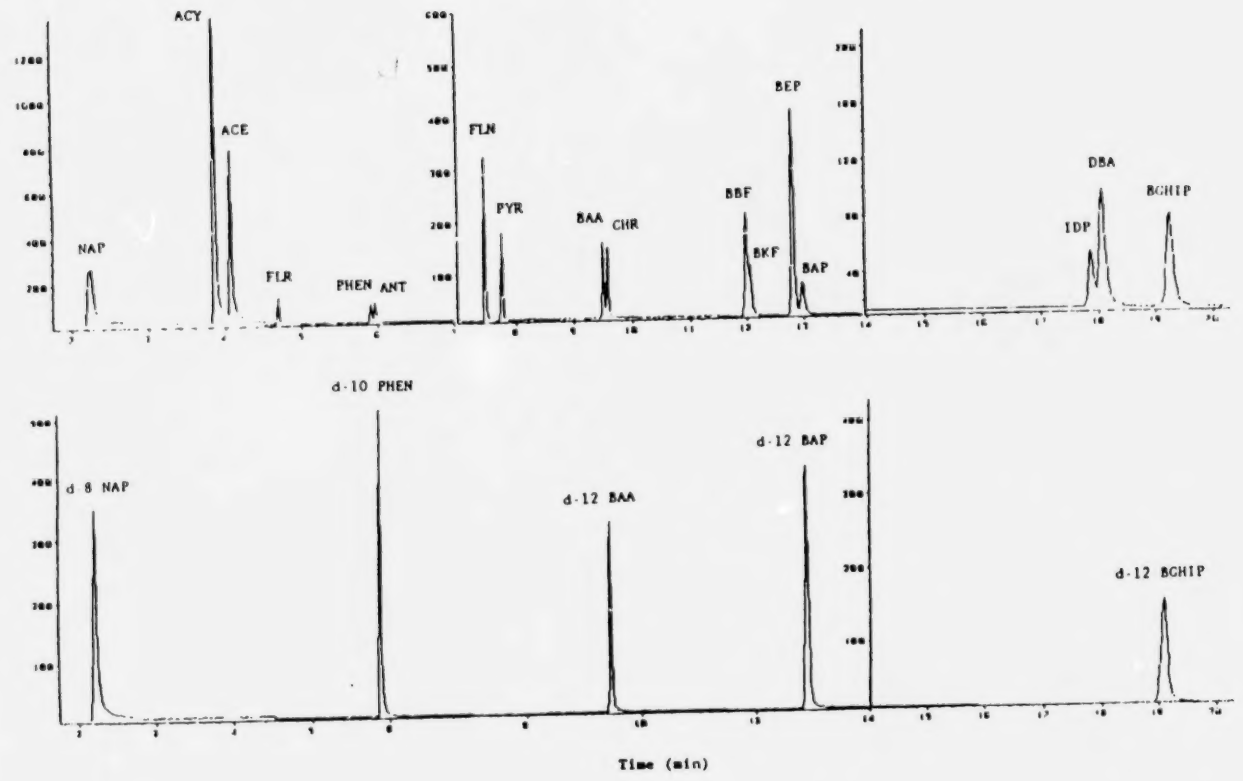


Figure 7. Chromatogram of 17 PAHs Using GC-Mass Selective Detector

TABLE 3.

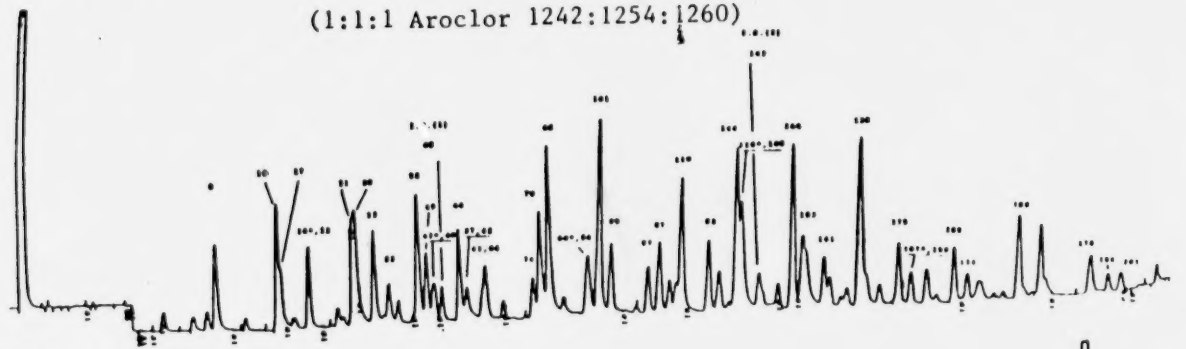
Chromatographic Conditions for Analysis of PAHs and Chlorinated Hydrocarbons

COLUMN			
Stationary Phase	5 % cross-linked phenyl methyl silicone (Hewlett-Packard 19091B)		
Length	25 meters		
i.d.	0.31 mm		
Film Thickness	0.52 um		
TEMPERATURE PROGRAM	**PCBs & Pesticides**	**Chlorinated Benzenes**	**PAHs**
Initial Temp. (°C)	150	50	125
Initial Time (min.)	1.0	3.0	0.5
Temp. Ramp (°C/min)	10 for 3 min. 1.3 to Final Temp.	10 for 2 min. 2.5 for 20 min. 3 for 30 min. 20 for 5 min.	20 to Final Temp.
Final Temp. (°C)	275	275	280
Run Time (min.)	70	60	22
GAS			
Carrier	Nitrogen	Nitrogen	Helium
Makeup	Nitrogen	Nitrogen	N/A
Carrier Flow (mL/min)	0.5	0.5	0.6
Makeup Flow (mL/min)	30	30	N/A
Injection Temp. (°C)	250	250	250
Detector Temp. (°C)	325	325	280
Detector Mode	ECD	ECD	Mass Spectrometer Operated in Selective Ion Monitoring Mode

FIGURE 8

Glass Capillary Gas Chromatograms with Electron Capture Detection of PCB Aroclor Mixtures

(1:1:1 Aroclor 1242:1254:1260)



(Sample SM 6265)

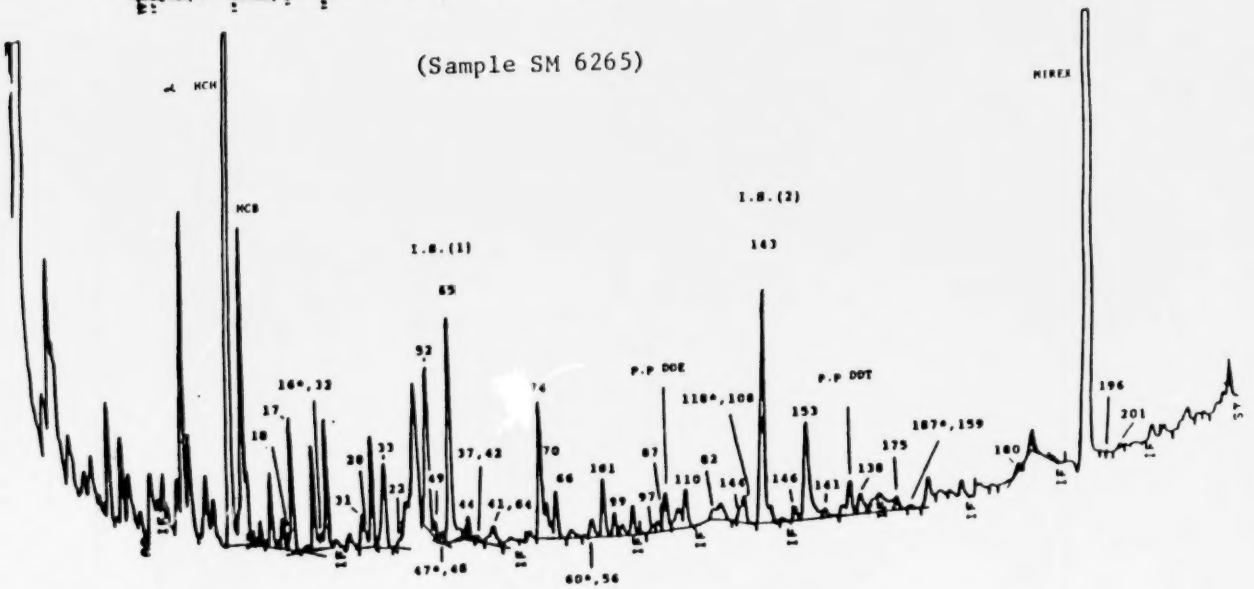


TABLE 4.

PCB Congener Numbers and Structures

Peak # (a)	Congener # IUPAC (b)		Structure
1	8		2,4'
2	18		2,2',5
3	17		2,2',4
4	16*,32	(16) (32)	2,2',3
			2,4',6
5	31		2,4',5
6	28		2,4,4'
7	33		2',3,4
8	22		2,3,4'
9	52		2,2',5,5'
10	49		2,2',4,5'
11	47,48	(47) (48)	2,2',4,4'
			2,2',4,5
12	44		2,2',3,5'
13	37,42	(37) (42)	3,4,4'
			2,2',3,4'
14	41*,64	(41) (64)	2,2',3,4
			2,3,4',6
15	74		2,4,4',5
16	70		2,3',4',5
17	66		2,3',4,4'
18	60*,56	(60) (56)	2,3,4,4'
			2,2',3',4'
19	101		2,2',4,5,5'
20	99		2,2',4,4',5
21	97		2,2',3',4,5
22	87		2,2',3,4,5'
23	110		2,3,3',4',6
24	82		2,2',3,3',4
25	144		2,2',3,4,5',6
26	118*,108	(118) (108)	2,3',4,4',5
			2,3,3',4,5'
27	146		2,2',3,4',5,5'
28	153		2,2',3,3',5,5'
29	141		2,2',3,4,5,5'
30	138		2,2',3,4,4',5'
31	175		2,2',3,3',4,5',6
32	187*,159	(187) (159)	2,2',3,4',5,5',6
			2,3,3',4,5,5'
33	185		2,2',3,4,5,5',6
34	174		2,2',3,3',4,5,6'
35	180		2,2',3,4,4',5,5'
36	170		2,2',3,3',4,4',5
37	196		2,2',3,3',4,4',5',6
38	201		2,2',3,3',4',5,5',6

(a) Peak number corresponds to the chronological order of elution under the chromatographic conditions used by this lab.

(b) If two congeners listed, they coelute with GC/ECD conditions of this lab. Dominant peak indicated with "*", if neither peak dominates both congeners listed.

The PCBs and pesticides beginning with sample period 6195 and all of the PAHs were quantified using the internal standard method. Response factors were calculated from calibration curves generated from standards which had been spiked with the same internal standards and run on the GC at the same time as the samples. Total PCB concentrations were calculated as the sum of the 38 PCB congeners of greatest weight fraction in Aroclor 1242, 1254 and 1260 appearing in the rain. Table 5 lists the compounds detected and analyzed in rain samples for this study. Fourteen compounds were selected for intercomparison of the four organic rain samplers based on their range of physical-chemical properties and their consistent appearance in collected precipitation.

TABLE 5

ORGANIC COMPOUNDS ANALYZED IN WET-ONLY PRECIPITATION

PAH

Naphthalene
Acenaphthylene
Acenaphthalene
Fluorene
*Phenanthrene
Anthracene
Fluoranthene
Pyrene
Benzo[a]anthracene
*Chrysene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[e]pyrene
*Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
*Benzo[ghi]perylene
Dibenzo[ah]anthracene
*Total PAHs

CHLORINATED BENZENES

1,2-Dichlorobenzene
1,3-Dichlorbenzene
1,4-Dichlorobenzene
*1,2,4-Trichlorobenzene

PCBs

38 PCB Congeners
including
* Congener 31 - 2,4',5-TriCB
* Congener 70 - 2,3',4',5-TetCB
* Congener 110 - 2,3,3'4',6-PentaCB
* Congener 138 - 2,2',3,4,4',5'-HxCB
* Congener 180 - 2,2,',3,4,4',5,5'-HeptaCB
* Total PCBs

CHLORINATED HYDROCARBONS

* Hexachlorobenzene - HCB
α - Hexachlorocyclohexane - HCH
β - Hexachlorohexane - HCH
δ - Hexachlorohexane - Lindane
Heptachlor
Heptachlor epoxide
Aldrin
Dieldrin
Endrin
* p,p'-DDE
p,p'-DDD; o,p'-DDD
p,p'-DDT; o,p'-DDT

* Compounds selected for intercomparison of samplers

Quality Assurance/Quality Control

The analytical procedure was characterized as to detection limits of the fourteen compounds, procedural blanks carried through the whole scheme, the recovery of compounds spiked into the resin or extracts, the recovery of surrogate compounds spiked into each sample and the ability of the XAD-2 resins to recover compounds of interest.

Detection limits (DL) may be statistically generated by repeated analysis of blanks and/or by characterization of the instrumental signal to noise ratio of blanks and low concentration standards. We have defined a "working" detection limit as the lowest quantifiable concentration of a specific analyte above the blank. The detection limits were estimated from repeated analysis of low concentration standards and samples. In general, the working DLs occurred in the following ranges: PAHs, 0.01 - 1.3 ng/L; PCBs, 0.001 - 0.03 ng/L for individual congeners and 0.04 to 0.54 ng/L for total PCBs; 0.005 - 0.07 ng/L for the chlorinated pesticides; 0.001 to 0.5 ng/L for the chlorinated benzenes. Table 6 gives the "working" DL's for 14 compounds selected for intercomparison of samplers. The DLs are based on an 8.0 L rain sample for the MIC samplers and 2.5 L for the modified RA sampler.

The characteristic concentration blank for the trace organic compounds of interest varies with the mode of isolation. The blanks reported here represent the average values determined from repeated injections of XAD-2 extract or DCM from the SM sample. These were obtained by deployment of the resin cartridges in the field and treating them as samples. The blank derived from the SM sampler

Table 6

Summary of Analytical Quality Control Data

Compound	Avg. Blank Conc. XAD-2	SM-DCM	"Working" DL	Avg. XAD-2 Recovery (%)
	(ng/L)			
Phenanthrene	0.9	0.3	0.2±0.17	69
Chrysene	0.3	0.3	0.2±0.15	
Benzo[a]pyrene	0.7	ND	0.12±0.13	73
Benzo[ghi]perylene	ND	0.1	0.37±0.31	75
Total PAHs	1.9	1.0	3.9±3.0	
1,2,4-TriClBenzene	0.8	0.1	0.013±0.007	95
HCB	0.027	0.006	0.005	86
p,p'-DDE	0.016	0.007	0.02	
Congener 31	0.03	0.014	0.009±0.006	92
Congener 70	0.022	0.01	0.008±0.005	
Congener 110	0.017	0.017	0.006±0.004	
Congener 138	0.015	0.012	0.005±0.004	
Congener 180	0.015	0.007	0.008±0.005	
Total PCBs	0.43	0.21	0.22±0.15	

* Blanks based on sample volume = 8.0 L.

represents DCM taken to the field and returned for analysis in the normal sample runs. Table 6 lists the contaminant blanks for the 14 compounds of interest for the resin and DCM matrices. In general, the blanks for SM sampler using batch DCM extraction were ≈ 50% of those for the XAD-2 cartridges. The range in blank values for the SM sampler were as follows: PAHs, 0.1 - 1.4 ng/L; PCBs, 0.001 - 0.04 ng/L for individual congeners and 0.15 - 0.3 ng/L for total PCBs; chlorinated pesticides, 0.001 - 0.5 ng/l; chlorinated benzenes, 0.02 - 0.6 ng/L. The blanks observed for the XAD-2 resins occurred in the range: PAHs, 0.1 - 1.7 ng/L; PCBs, 0.001 - 0.2 ng/L for individual congeners and 0.2 - 0.7 ng/L for total PCBs; chlorinated pesticides, 0.001 - 0.4 ng/L; chlorinated benzenes, 0.01 - 1.9 ng/L. These values assume a sample volume of 8.0 L, the average volume collected by the MIC sampler. For the RA sampler, multiply these blanks by 3.2 to correspond to a sample volume of 2.5 L. The naphthalene blank on the XAD-2 resin was large and precluded any quantification. In general, blanks were less than 10 to 20% of the analyte in the sample, and often were much less. The blank values were sufficiently variable to preclude subtraction from analyte mass in the sample.

Surrogate compounds were spiked into the DCM extract of each SM sample and each XAD-2 resin from the RM, FM and RA samples to monitor procedural recoveries. Table 7 lists the recovery of the 3 surrrogate compounds applied to the solvent (SM), resin and filter samples. In general, the surrogate recoveries averaged 60 to 80% over the course of the project. Analyte concentrations were not corrected for sample recoveries. Samples and standards analyzed repeatedly yielded average

Table 7

Recovery of Procedural Surrogates
(%)

Compounds	Solvent (SM)	XAD-2 (RA,RM,FM)	Filter (FM-F)
d-10 Anthracene	60±9	60±14	65±14
1,4-Dibromobenzene	65±9	74±16	72±9
Mirex (ext. std.)	64±10	73±14	66±6
Mirex (int. std.)	54±17	62±19	68±27

relative precision of ±5-20% depending on compound and concentration.

The ability of XAD-2 resin cartridges to concentrate CHs and PAHs from rain water was evaluated in laboratory experiments. The organic compounds of interest were added to duplicate, clean, empty 20-L glass carboys and the solvent allowed to evaporate. Then the carboys were filled with Milli-Q water, covered with aluminum foil and allowed to equilibrate for almost five days at room temperature. The carboy at the outset contained ≈100 ng/L PCBs as Aroclor 1242, 5-50 ng/L of the chlorinated benzenes and 50-100 ng/L of the PAHs. The loss of some organic compounds by volatilization and adsorption to the glass walls was expected. Prior to the running of the experiment, each spiked carboy was sampled for determination of the water concentration of each CH and PAH. The spiked solutions were pumped through XAD-2 resin cartridges connected in series at flow rates of about 35 to 50 mL/min in replicate runs. Recoveries of surrogates spiked into the water were: 1,4 Dibromobenzene, 67 ± 9%; Mirex, 82 ± 10% and d-10 Anthracene, 69 ± 7%. The chlorinated benzenes were quantitatively recovered in the experiments with about 3 to 8% occurring in the backup XAD-2 column. PCB congeners in Aroclor 1242 were also quantitatively recovered with less than 2 - 5% occurring in the backup column. Five PAHs in the spiked solution were recovered in the range of 62 - 100% on the first column and quantitatively recovered in the combination of sequential columns. HCB, Lindane and p,p'-DDD were recovered quantitatively on the first XAD-2 column but chromatographic interferences precluded the analysis of p,p'-DDE and α-HCH in the experiments. These experiments show that XAD-2 resins in the

configuration used in the field and slightly elevated concentrations are effective at isolating the compounds of interest.

RESULTS AND DISCUSSION

Criteria for Precipitation Collectors

Criteria to consider in constructing, modifying or selecting precipitation samplers for assessing atmospheric inputs of trace contaminants have been summarized in several publications (Eisenreich et al., 1980; Strachan and Huneault, 1984; Pankow et al., 1984; Murphy, 1987). Wet-only, precipitation-activated collectors should be utilized for wet deposition measurement. The sample receptors should be protected from sedimentary, turbulent and gaseous inputs when it is not raining, and should be constructed of carefully selected materials so that inadvertent loss or addition of a trace chemical is minimized. Depending upon particular pollutants of interest, materials such as stainless steel and glass may not always be appropriate. In general, the use of non-contaminating polymeric surfaces is recommended for many applications. For trace organic compounds in rain, use of glass, stainless-steel or Teflon-coated surfaces have generally been recommended.

Ideally, precipitation collectors for assessing organic inputs from the atmosphere should have the following characteristics:

1. Collects wet-only precipitation.

2. Collector possesses large surface area (≈ 0.2 to 1.0 m^2).
3. Collection/storage surface should be non-contaminating, non-adsorbing and made of stainless-steel, glass or Teflon.
4. Collector has a fast responding and tightly-sealing covering mechanism.
5. Collector should be suitable for unattended operation over periods of 2 to 4 weeks.
6. Collector will undoubtedly require access to electricity.
7. Initial stages of the rain events must be collected.
8. Collector should be versatile such that organic compounds differing in concentration, physical/chemical properties and speciation in rain may be efficiently collected and isolated.

The MIC and Aerochem Metrics samplers selected and modified for study in this project differ in their surface area, type of collection surface, mode of organic compound isolation and in-line filtration. All the samplers collect wet-only precipitation as water-sensitive sensors activate movement of the mechanical arm to open the collection funnel. The samplers are intercompared on the basis of rain collection efficiency, mechanical and operational characteristics and ability to provide precise estimates of organic concentrations and fluxes.

Rain Collection Efficiency

The ability of wet-only precipitation samplers to efficiently collect rain under environmental conditions is crucial to determining accurate concentrations and fluxes. The samplers were deployed in the field on 8 May, 1986 with the first rain sample collected on 13 May, 1986 (Julian date 133) and the last rain sample collected on 13 October, 1986 (Julian date 286). The samplers were deployed in early autumn of 1985 only as a test run for the 1986 field season. The rainfall measured with the two rain gauges averaged 55.1 cm with less than 2% difference between gauges. A continuous recording rain gauge

at a Minnesota Pollution Control Agency site located within 50 m showed cumulative rainfall of 55 cm over the same period.

The collection efficiency of each sampler was determined by comparison to the theoretical collection efficiency based on the duplicate rain gauges located on the sampling platform. Figure 9 shows the rain collection efficiencies of the SM, RM, FM and RA rain samplers compared to the theoretical value. Excluding the periods when mechanical malfunctions or vandalism occurred, the average rain collection efficiency was ≈ 95% (Table 8). Including these anomolous periods, collection efficiencies were reduced to 80 - 90%. The RA sampler suffered from early problems with the precipitation sensor. Once replaced, the rain collection efficiency increased from 83% prior to the sensor being changed to 101% after. Large deviations from 100% collection efficiency for all samplers resulted from blown fuses, lossened nuts on rotating arm and evaporation of water when flow through the resin cartridge was hindered. A special problem exhibited for the SM sampler occurs in rainfall volumes exceeding 8 L. In this case, excess water is lost to drainage without being measured. This problem can easily be solved by increasing storage volume in the SM sampler.

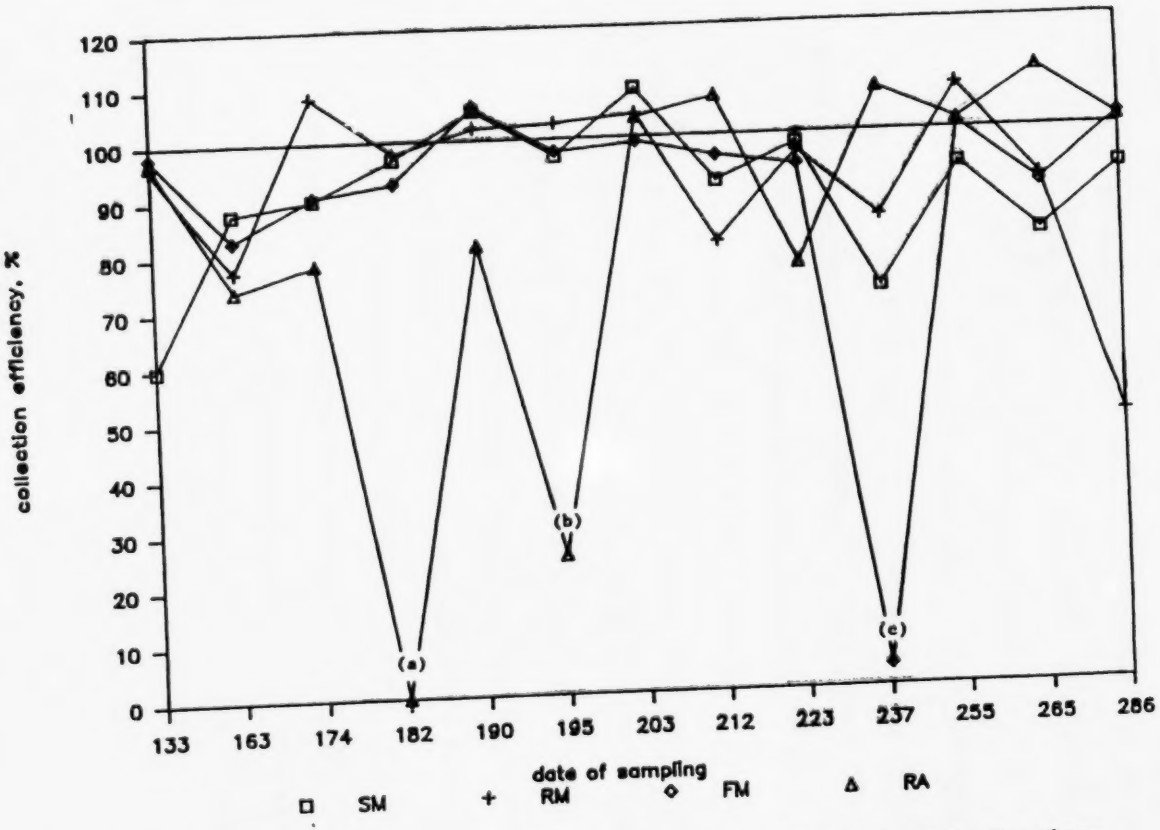


Figure 9. Rain Collection Efficiency of the SM, RM, FM, and RA Wet-Only Rain Samplers
(a) carboy empty, cause unknown (b) moisture sensor malfunction (c) blown fuse

Table 8

Rain Sampler Collection Efficiency
(%)

Collection Efficiency	Rain Sampler SM	RM	FM	RA
Overall Average	90	92	89	82
Excluding malfunctions	94	96	96	95
Standard Deviation	10	10	6	14

Figures 10-13 directly show the collection efficiencies by sampler for each rain sample period in 1986. The upper plot represents a comparison of collected to theoretical rain volume with the line depicting a 1:1 relationship. Points plotted below the 1:1 line represent those time periods in which collected rain volume was less than that inferred from the average of the two rain gauges. The lower plot represents the positive or negative deviation of each sampler volume compared to the theoretical for each period. The overall sampler performance occurs in the decreasing order RM > SM > FM > RA. We conclude that properly operating precipitation samplers of the MIC type are effective in the collection of falling rain. The differences in performance are attributed to malfunctions in operation.

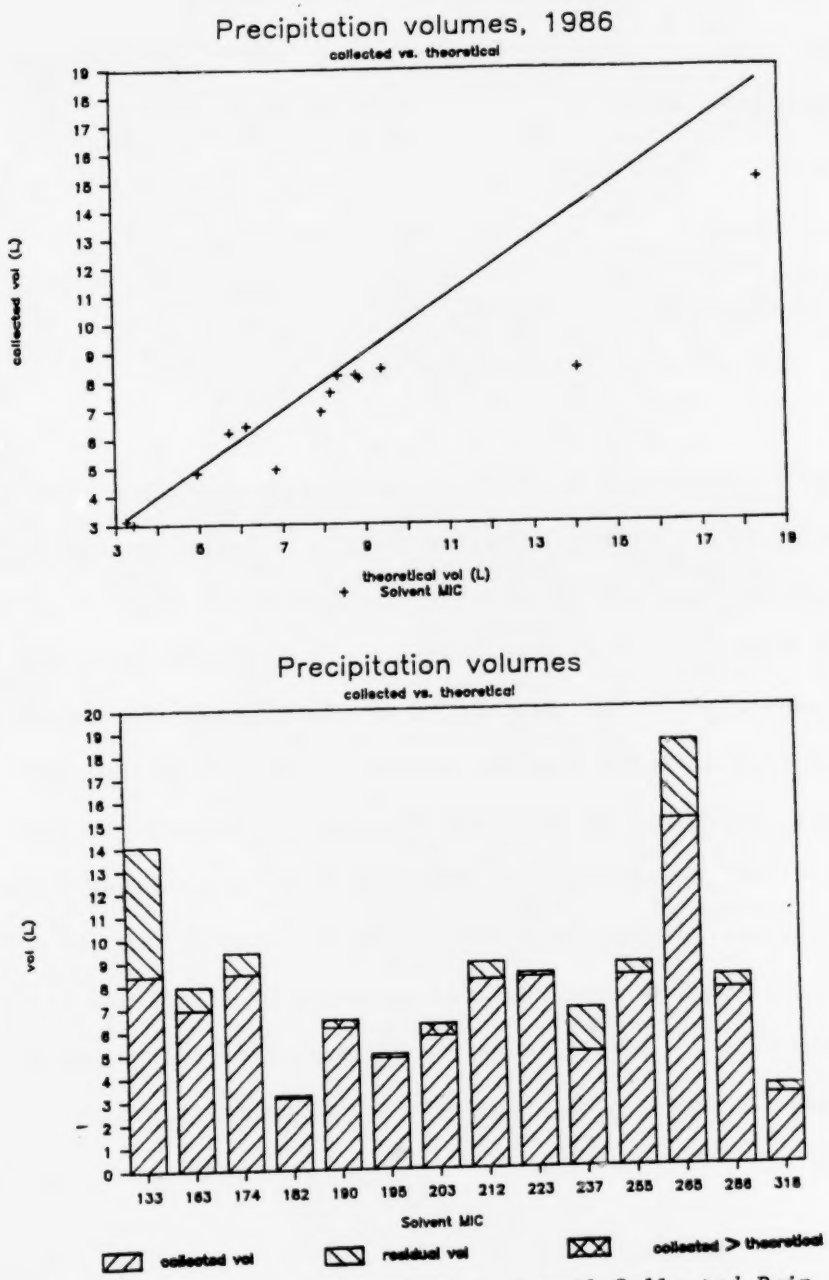


Figure 10. Comparison of Theoretical to Actual Collected Rain Volume for the Solvent MIC (SM) Sampler

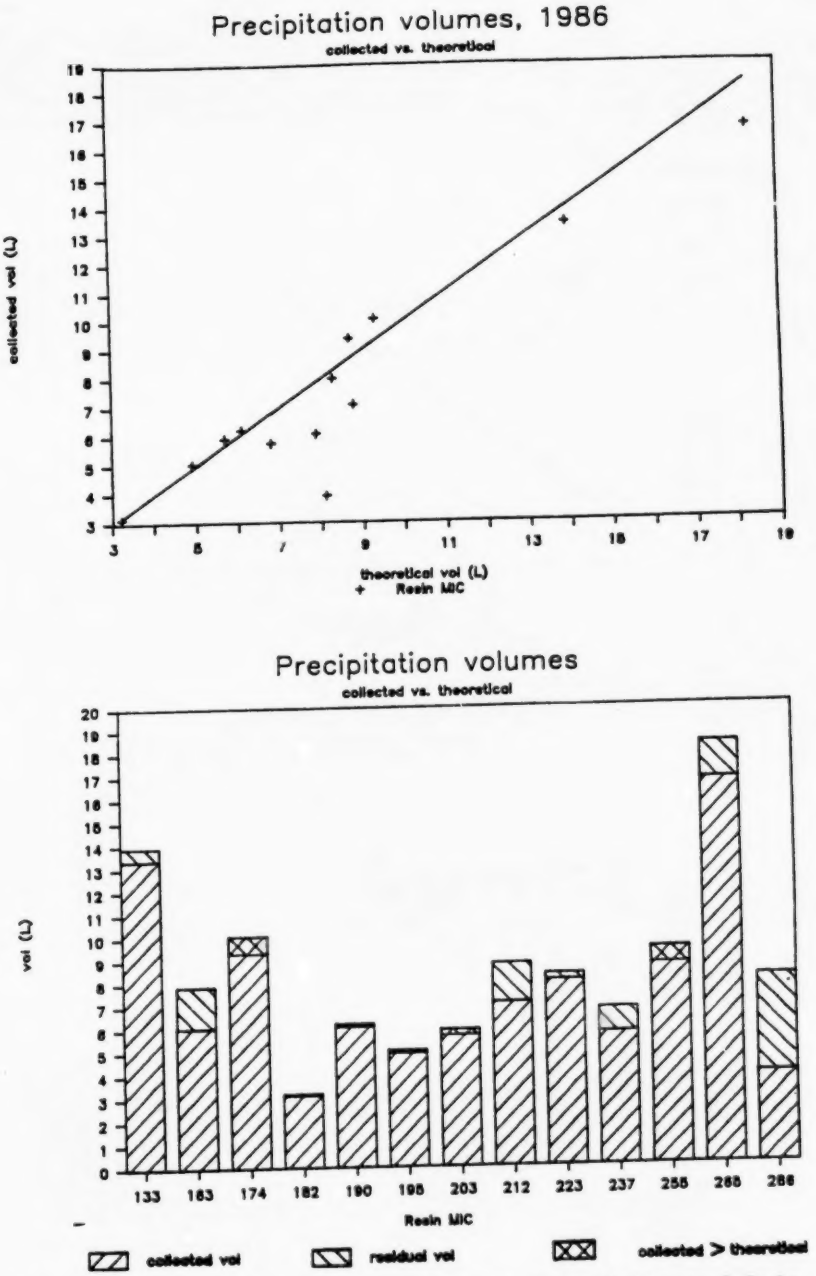


Figure 11. Comparison of Theoretical to Actual Collected Rain Volume for the Resin MIC (RM) Sampler

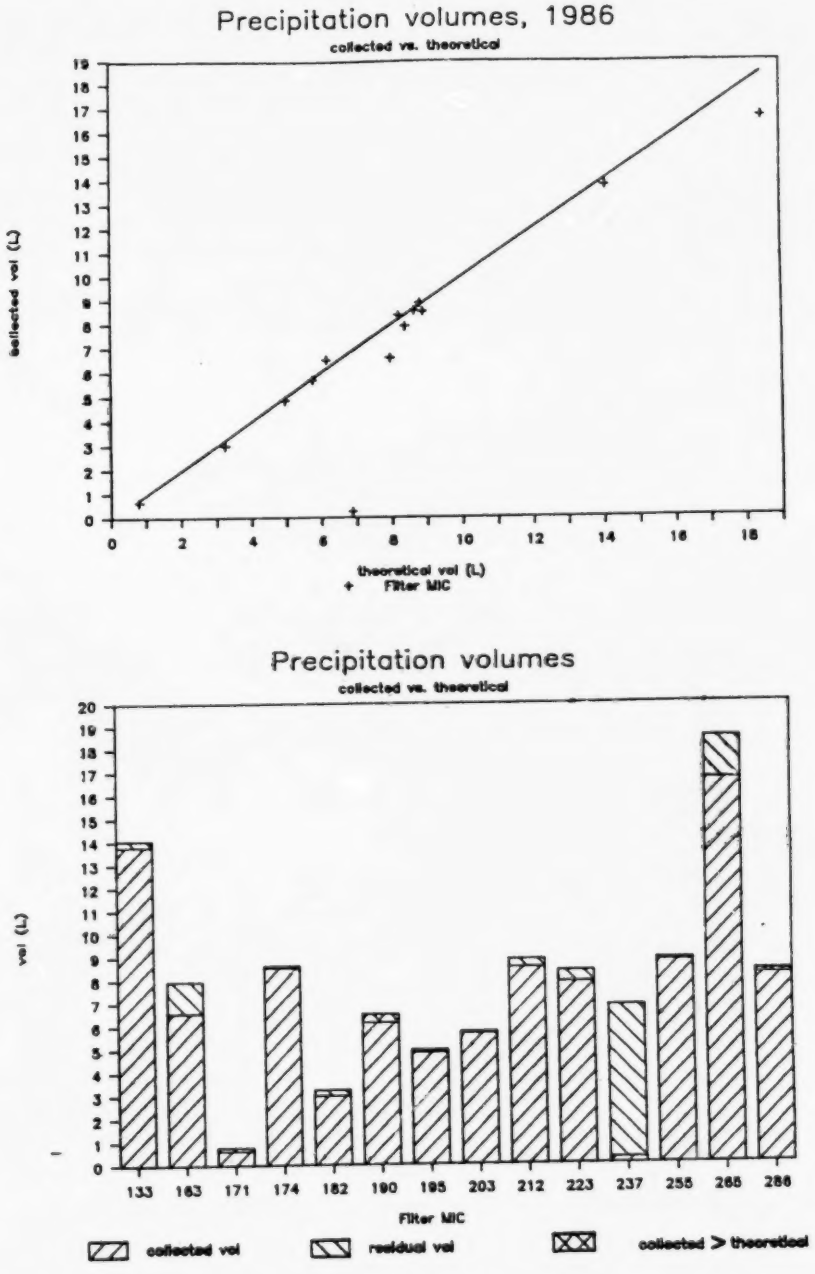


Figure 12. Comparison of Theoretical to Actual Collected Rain Volume for the Filter MIC (FM) Sampler

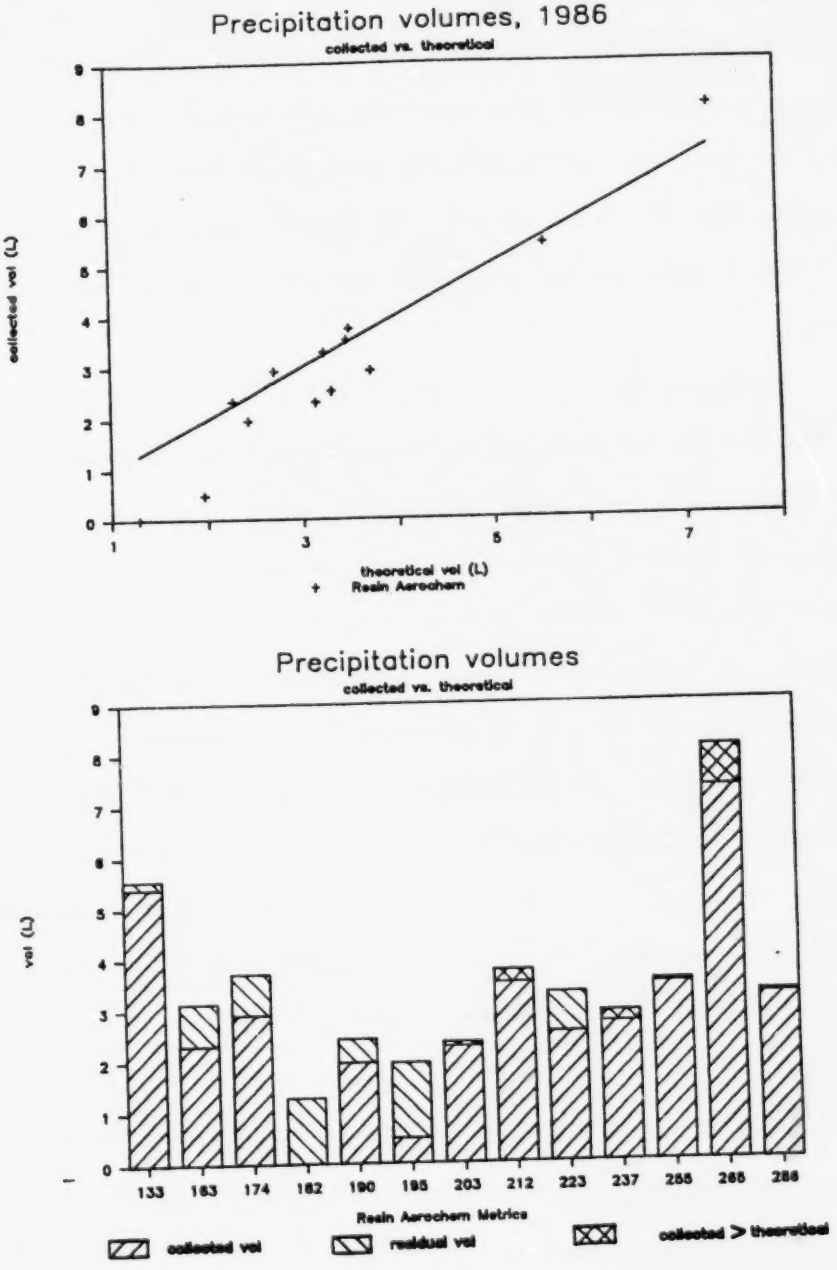


Figure 13. Comparison of Theoretical to Actual Collected Rain Volume for the Resin Aerochem Metrics (RA) Sampler

Organic Contaminant Collection

The ability of the four samplers to collect trace organic compounds in rainfall was evaluated for fourteen specific compounds. Table 9 presents the volume-weighted mean concentrations of the 14 compounds collected and analyzed, and also the propagated error for each. The volume-weighted mean (VWM) concentration was calculated as follows:

$$VWM_i = \sum M_{ij} / \sum V_j = \sum (C_i x V_j) / \sum V_j \qquad (12)$$

where VWM_i is the volume-weighted concentration of compound i, M_{ij} is the mass of compound i in the jth rain interval, V is the volume of the jth rain interval and C_i is the concentration of compound i in each rain interval. The propagated errors listed in Table 9 were calculated in the method outlined by Shoemaker et al. (1974); a full derivation of the technique is presented in the Appendix.

The 14 compounds differ in their physical-chemical properties, speciation in the atmosphere, and concentration in collected rain. Total PAH VWM concentrations range from 44.4 to 60.5 ng/L depending on sampler and total PCBs ranged from 2.3 to 2.8 ng/L. The propagated errors varied with compound and occurred generally in the range of 10 to 30%.

The primary question addressed by this data set is whether VWM concentrations of each of 14 compounds observed in the SM, RM, FM and RA samplers were significantly different. A related question is whether any significant differences could be attributed to characteristics of the rain samplers and/or compounds. Given the nature of the data set, the approach chosen to answer these questions

Table 9

Volume-Weighted Mean Concentrations for Fourteen Organic Compounds in Wet-Only Precipitation - 1986 (ng/L)

Compound	Sampler			
	SM	RM	FM	RA
Phenanthrene	8.6±2.1	15.4±3.8	8.8±2.2	11.2±2.8
Chrysene	6.1±1.1	6.5±1.2	5.1±0.9	5.6±1.0
Benzo[a]pyrene	1.4±0.4	3.3±1.0	2.9±0.9	3.5±1.1
Benzo[ghi]perylene	2.2±1.0	1.9±0.9	1.4±0.7	1.5±0.7
Total PAHs	53.9	60.5	44.4	54.2
1,2,4-Trichloro benzene	11.7±1.2	4.1±0.4	10.7±1.1	10.7±1.1
Hexachlorobenzene	0.57±.07	0.18±.02	0.12±.02	0.48±.06
p,p'-DDE	1.1±.46	2.1±.85	0.33±.13	0.92±.38
Total PCBs	2.6±0.6	2.3±0.5	2.7±0.6	2.8±0.6
Congener 31	0.16±.03	0.12±.02	0.19±.04	0.13±.03
Congener 70	0.16±.05	0.09±.03	0.09±.03	0.14±.04
Congener 110	0.15±.04	0.11±.03	0.09±0.2	0.11±.03
Congener 138	0.05±.02	0.06±.02	0.09±.03	0.04±.01
Congener 180	0.024±.005	0.031±.006	0.07±.02	0.08±.02

was to calculate the volume-weighted mean concentrations and associated propogated errors. Parameters used to estimate the propagated error were uncertainties in the measurement of rain volume, determined masses of individual compounds, and precision of analytical measurements. The simple criterion applied to the primary question is whether the error bars calculated as propagated error overlapped for individual compounds observed for different samplers.

Figure 14 presents the VWM -concentrations and propagated errors for phenanthrene, chrysene, benzo[a]pyrene and benzo[ghi]perylene in the SM, RM, FM and RA samplers. In general, the error bars for the VWM concentrations of the compounds overlapped exhibiting no significant differences. The only possible exception is benzo[a]pyrene in the SM sampler exhibiting a VWM concentration about 50% of those observed for the other samplers. The primary difference in the SM sampler compared to the others is the mode of compound isolation; the SM sampler employs passive batch extraction with DCM in the field whereas the others employ XAD-2 resin cartridges. The SM has a stainless-steel surface (same as the RA sampler) which did not exhibit a widely different VWM concentration. Neither lost rain volume nor occurrence of benzo[a]pyrene explain the difference since substantial variations were not observed for other compounds.

Figure 15 presents the VWM concentrations and propagated errors for a group of chlorinated hydrocarbons including 1,2,4-trichlorobenzene (TriCB), hexachlorobenzene (HCB), p,p'-DDE, two PCB congeners having 4 and 5 chlorines and total PCBs. Again the VWM concentrations for most of the compounds and samplers are not

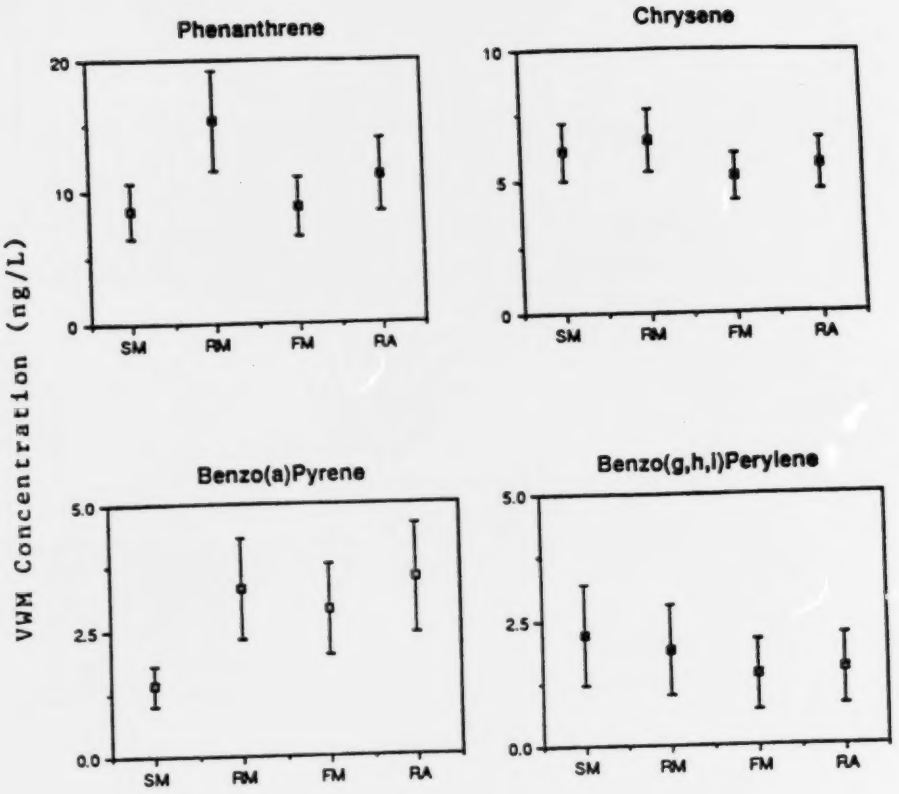


Figure 14. Volume-Weighted Mean Concentrations (VWM) and Propagated Errors of Four PAHs for the SM, RM, FM and RA Samplers

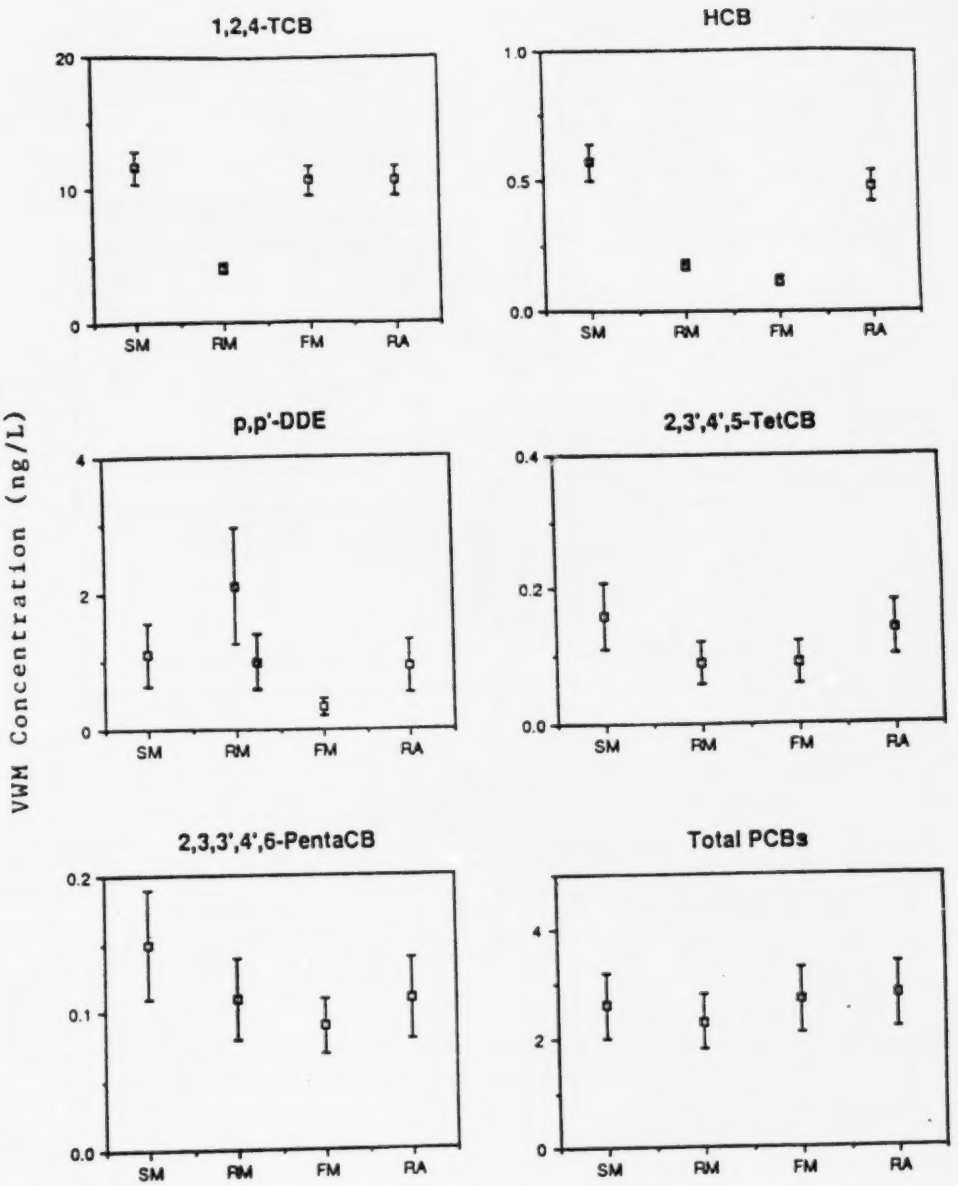


Figure 15. Volume-Weighted Mean Concentrations (VWM) and Propagated Errors of Six Chlorinated Hydrocarbons for the SM, RM, FM and RA Samplers

significantly different. Exceptions to this rule are TriCB in the RM sampler and HCB for which VWM concentrations stratify into two groups differing in concentration by a factor of ≈ 2. The resin MIC sampler occassionally had standing water in the funnel due to a backup in the resin column. This may have resulted in enhanced losses of TriCB by volatilization. The FM sampler, identical to the RM sampler except for the presence of an in-line filter, does not exhibit similarly low values. The low values of RM and FM compared to the SM and RA samplers may be due to the clogging problem noted above permitting losses to volatilization. Losses to the collector surface cannot give the same results since the surface was rinsed and the rinse analyzed with the resin. The RM and FM samplers both have Teflon surfaces which may in some cases cause problems with sorption. Compounds having lower aqueous solubilities and vapor pressures might be expected to exhibit more severe sorption problems; they apparently do not.

The VWM concentrations for p,p'-DDE, 2,3',4',5-TetCB, 2,3,3',4',6'-PentaCB and total PCBs across samplers are not significantly different. The lower VWM concentration for p,p'-DDE was used in the sampler intercomparison since only one very high value contributed to the difference in VWMs.

These results are consistent with the hypothesis that the SM, RM, FM and RA samplers are equally capable of providing comparable concentration data when expressed as VWMs. We suggest that significant differences in the VWMs between samplers may be mostly due to rain water being trapped in the funnel rather than the rain

reservoir and subjected to volatilization. This problem is largely restricted to the resin samplers. Future samplers employing resin cartridges should be equipped with small in-line peristaltic pumps linked to the funnel covering mechanism or activated by a flow or volume sensor.

Volume-weighted mean concentrations were calculated for all PAHs, PCBs and chlorinated benzenes and pesticides analyzed in 1986 rain. Figure 16A shows a comparison between the VWMs of 16 PAHs for the samplers with XAD-2 resins as the mode of compound isolation. There is generally less than a 20% difference between the VWM concentrations of the RM,FM and RA samplers. The biggest difference in VWMs occurs for phenanthrene where the RM, FM and RA samplers give concentrations of 15.3, 8.8 and 11.4 ng/L. Differences are not attributed to the relative concentrations of PAH in rain or physical-chemical properties of the compounds. Figure 16B shows a comparison of the VWM of the total sample population and the values exhibited for the solvent MIC or SM sampler. The agreement in all cases is very good with the resin-based samplers providing on average 5-10% higher VWM concentration compared to the SM sampler. No statistical difference was observed in this comparison between the solvent and resin samplers for isolating PAHs from rain.

Figure 17 compares the VWM concentrations of 27 PCB congeners ranging from 2 to 6 chlorines in the samplers employing only the resin cartridges (RM, FM, RA). Observed VWM concentrations range from ≈ 0.01 - 0.03 ng/L for congener 201 to 0.1 - 0.26 ng/L for congener 33. In general, the FM and RA samplers exhibit an equal number of highest

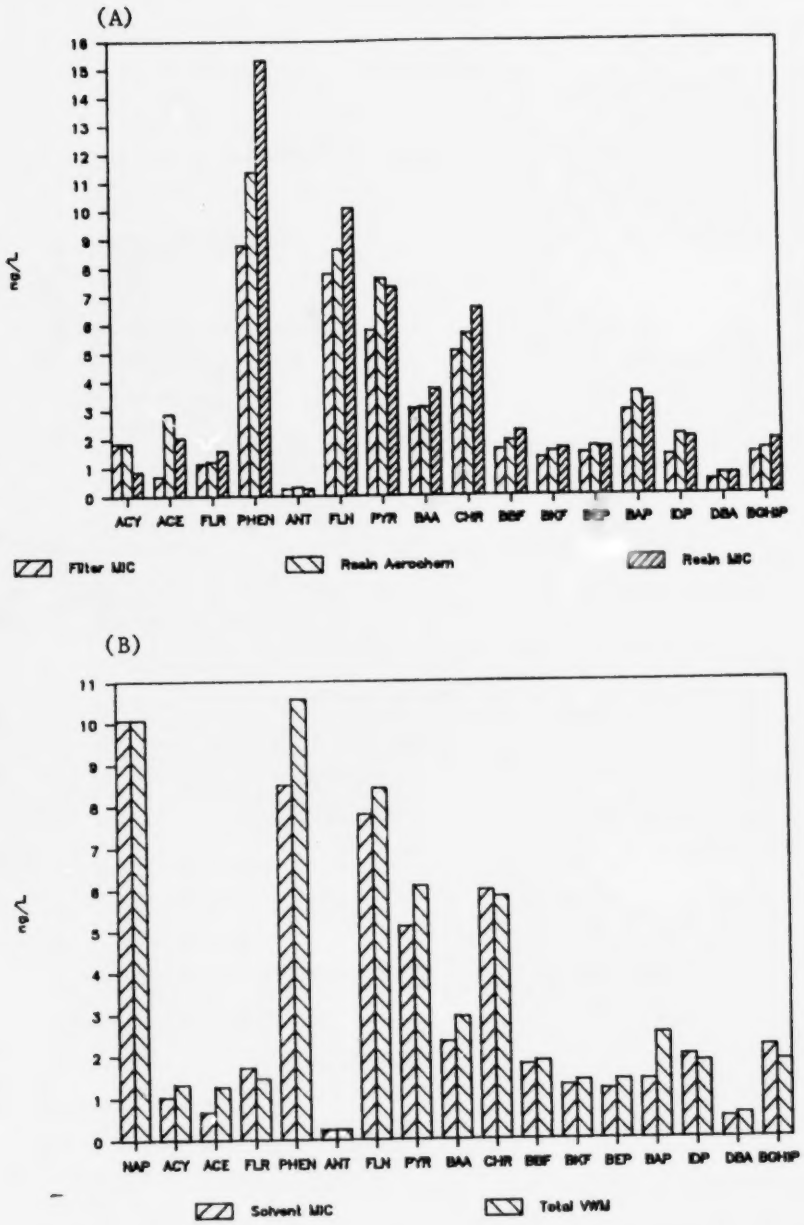

(A)
ng/L
ACY ACE FLR PHEN ANT FLN PYR BAA CHR BBF BKF BEP BAP IDP DBA BGHIP
Filter MIC
Resin Aerochem
Resin MIC
(B)
ng/L
NAP ACY ACE FLR PHEN ANT FLN PYR BAA CHR BBF BKF BEP BAP IDP DBA BGHIP
Solvent MIC
Total VWM

Figure 16. Comparison of Volume-Weighted Mean Concentrations (VWM) for 17 PAHs Between the RM, FM and RA Samplers (A) and Between the SM and All Samplers (B)

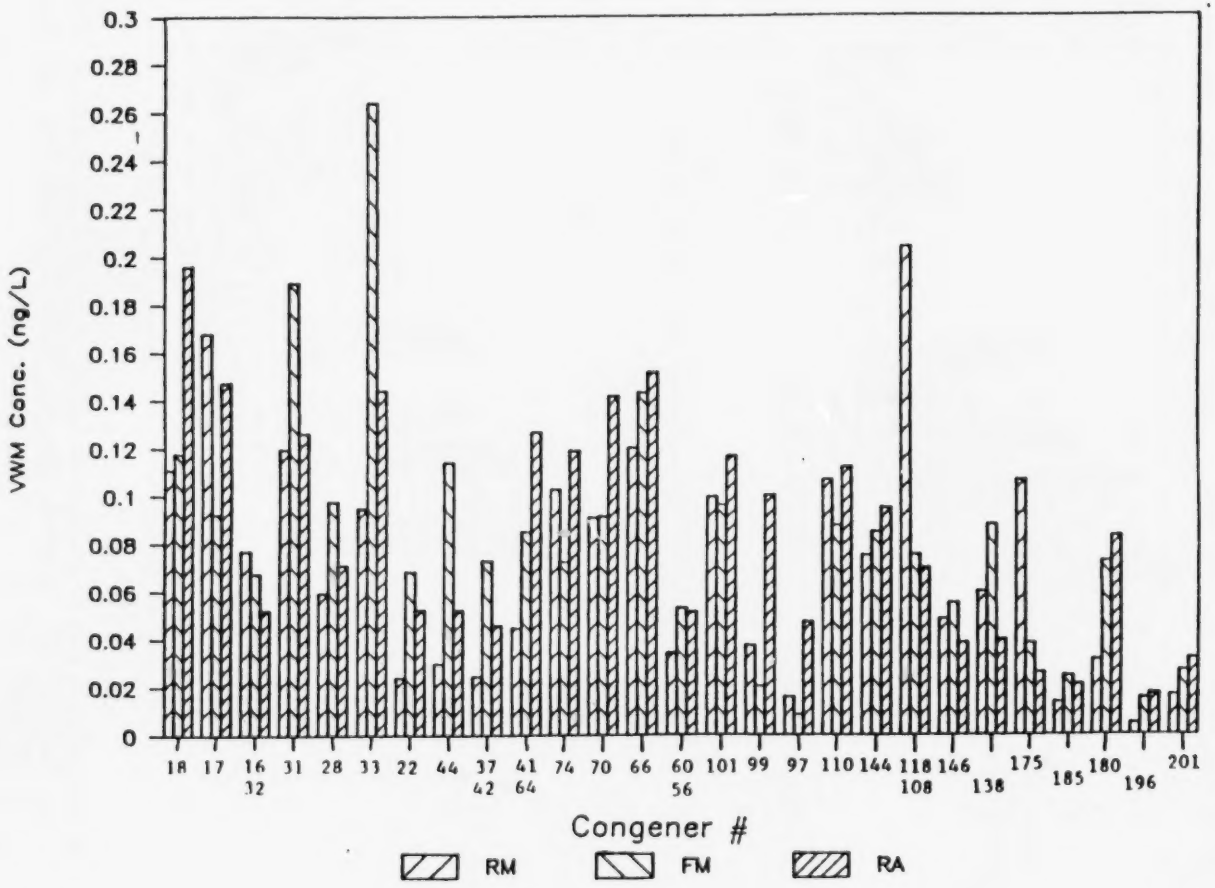


Figure 17. Comparison of Volume-Weighted Mean Concentrations (VWM) for 27 PCB Congeners for the RM, FM, and RA Samplers

VWMs and the RM sampler the highest number of low VWMs. This pattern suggests that the resin MIC (RM) sampler is less effective than the other resin samplers in isolating PCB congeners from rain. The reason for this observation is not clear. Although there are 50 to 150% differences in VWMs of individual PCB congeners across the resin samplers, the values of total PCBs are not significantly different (Figure 15). The RM sampler has a Teflon collection surface, a glass reservoir below the funnel and an XAD-2 resin cartridge. The FM sampler also has a Teflon collection surface and an XAD-2 resin cartridge but no glass reservoir and an in-line filter. The RA sampler has a stainless steel collection surface, a glass reservoir and an XAD-2 resin cartridge. The lower collection efficiency of PCB congeners for the RM sampler compared to the FM sampler may be due to passage of some fine particles through the resin cartridge along with increased retention by the filter/resin cartridge combination. Surface effects and lack of retention and recovery of dissolved PCB congeners by the resin cartridges apparently do not explain the results.

Figure 18 gives a direct comparison between the VWMs of individual PCB congeners for the SM sampler and the sum of all samplers. There are an approximate equal number of PCB congeners for which the SM sampler provides higher values as when it provides lower values. The difference in VWMs between the two types of samplers varies in general between 20 and 50%. All rain samplers show a predominance of 2 through 5 chlorinated PCBs at the expense of low quantities of higher chlorinated species. This pattern is similar to

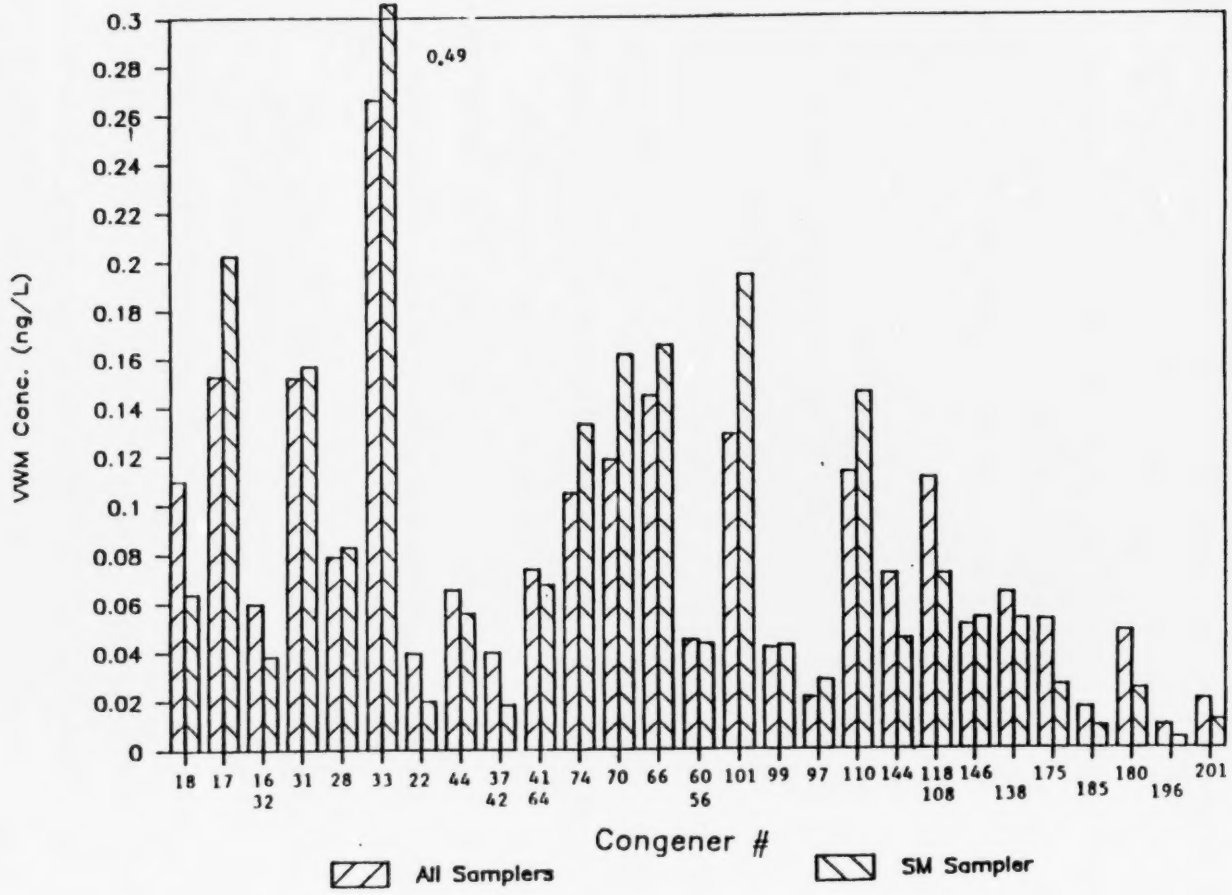


Figure 18. Comparison of Volume-Weighted Mean Concentrations (VWM) for 27 PCB Congeners Between the SM Sampler and All Samplers

that observed in air samples collected over Lake Superior during 1986 and proximate surface waters (J.E. Baker and S.J. Eisenreich, University of Minnesota, unpublished results).

Comparisons of VWM concentrations of organic compounds collected by the four samplers provides some insight as to their overall behavior. The results presented thus far suggest that the organic compound collection efficiency for the four samplers is not significantly different in assessing annual values and atmospheric fluxes. However it does not account for variations in compound collection efficiency in the same rain periods. To evaluate this phenomenon, the concentrations of selected PAHs and PCB congeners in 1986 rain events are presented followed by a one-way ANOVA comparison of compound behavior. The question being addressed is: do event-to-event variations in compound concentration show a statistically significant difference in a sampler's ability to collect organic compounds in rain.

Figure 19 shows event-to-event variations in rain concentration of phenanthrene, chrysene, benzo[a]pyrene, benzo[ghi]perylene and $\sum$ PAHs for the four samplers in 1986. Phenanthrene dominated the PAH distribution representing a relatively constant 20 to 25% of the $\sum$ PAH while chrysene represented a constant 10% of the total. This distribution is not unlike distributions observed in rain samples collected on Isle Royale in Lake Superior (McVeety and Hites, 1987) and in air over Lake Superior (Baker and Eisenreich, unpublished results). Phenanthrene and benzo[ghi]perylene concentrations are relatively uniform over the sampling period whereas the other PAHs

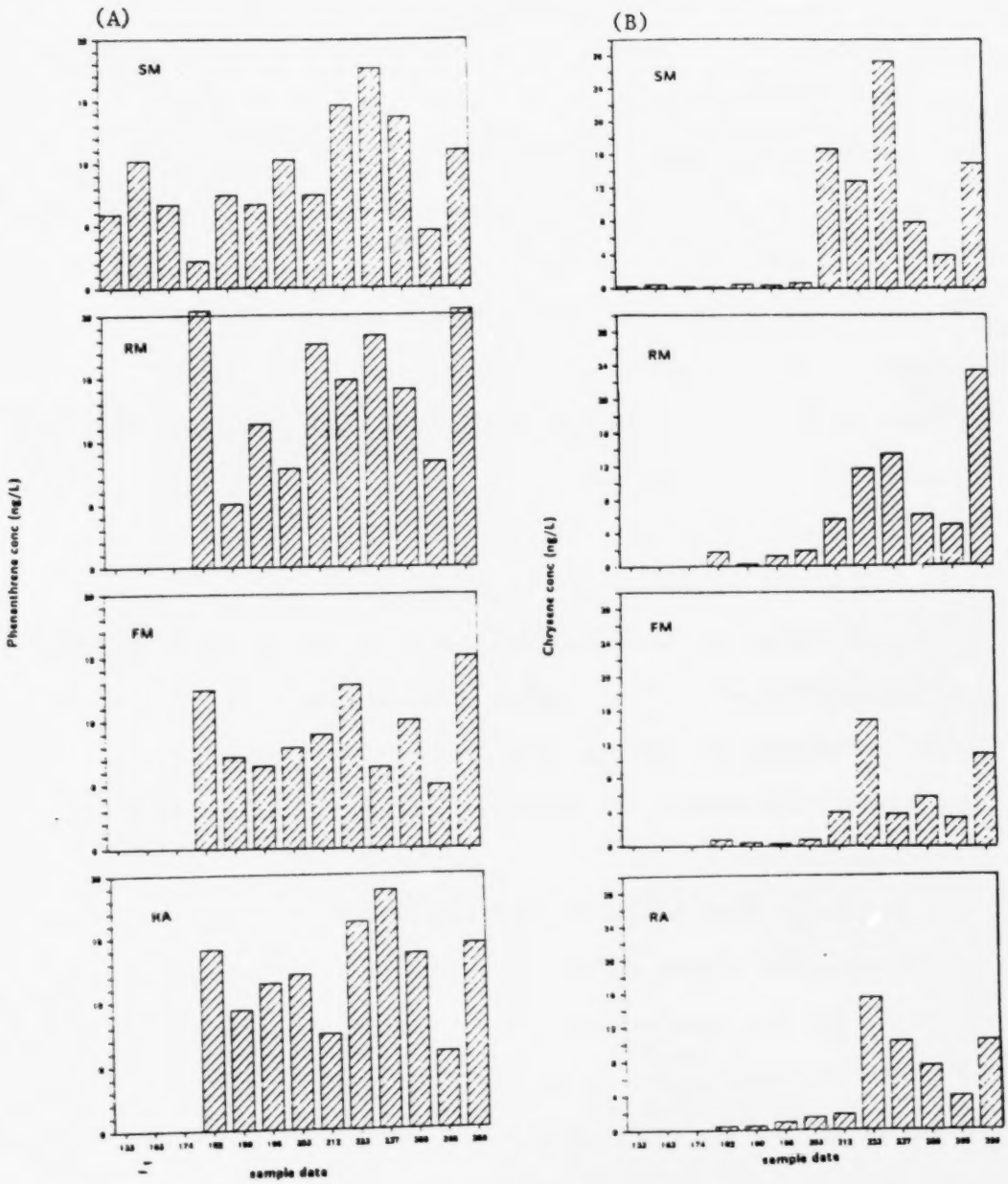
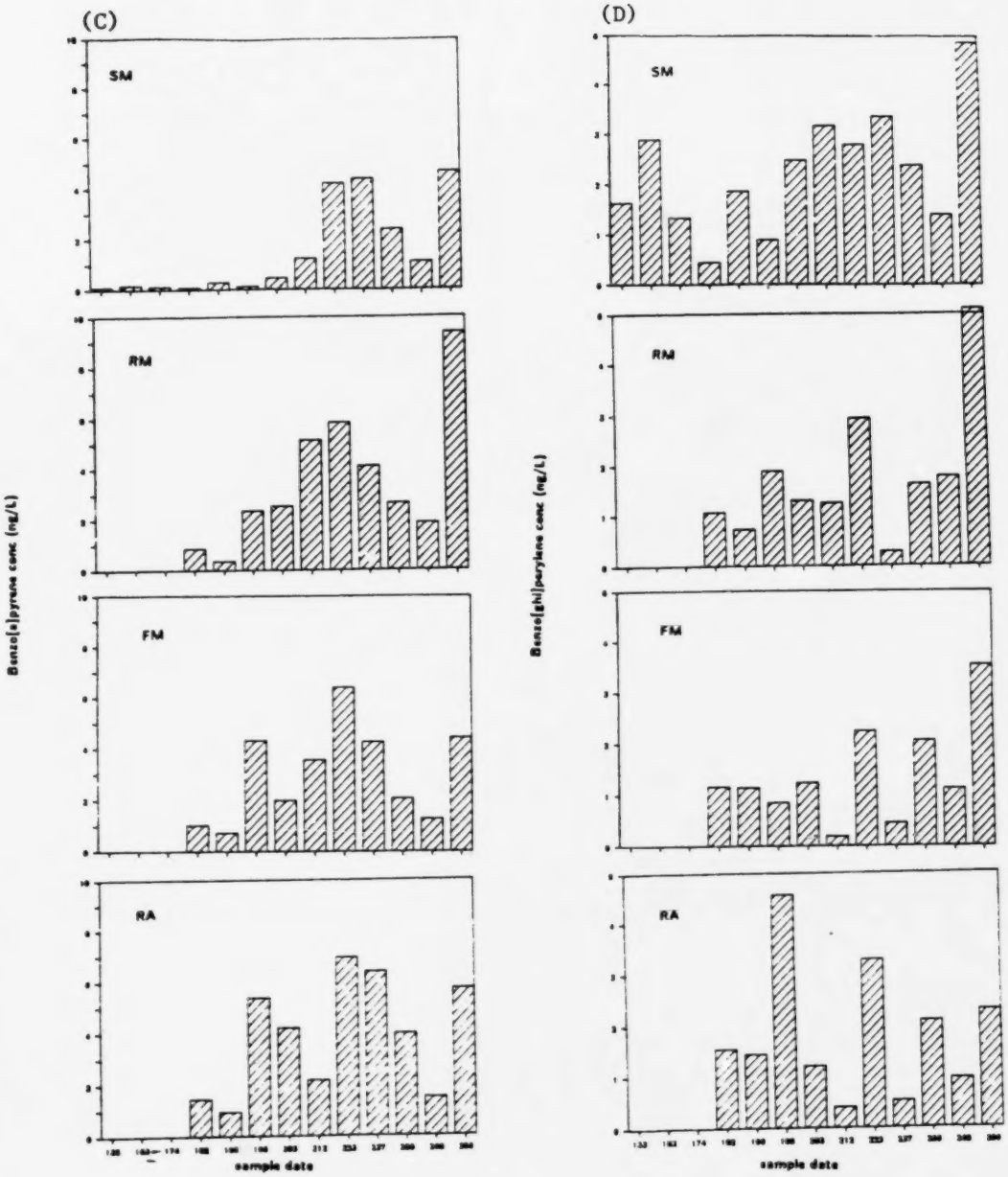


Figure 19. Temporal Concentration Variations for Selected PAH Compounds Observed in the SM, RM, FM and RA Samplers (A): Phenanthrene (B): Chrysene (C): Benzo(a)pyrene (D): Benzo(ghi)perylene (E): Total PAHs


(C)
(D)
SM
RM
FM
RA
Benzo[e]pyrene conc (ng/L)
Benzo[ghi]perylene conc (ng/L)
sample date
sample date

(E)

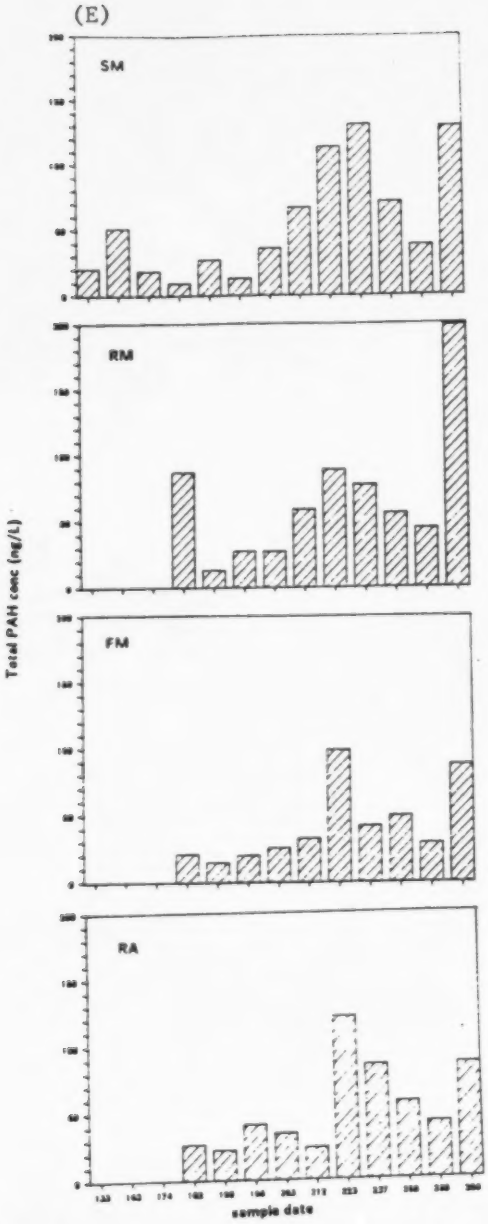


exhibit increasing concentrations from spring to autumn.

Figure 20 show shows event-to-event variations in rain concentrations of five PCB congeners and $\sum$ PCB for the four samplers in 1986. There are relatively large variations in PCB congener concentrations from sampler-to-sampler sometimes approaching 100% and variation in concentrations over the sampling period within each sampler. These results will be examined in a subsequent paper on concentrations and fluxes of PAHs and chlorinated hydrocarbons in rain.

A one-way ANOVA comparison of the fourteen selected compounds was conducted to test the null hypothesis that there is no difference between sampler behavior based on the event-to-event variations. The ANOVA calculations on the log transformed data are presented in Table 10. The mean square in column 1 represents the variance between samplers and the mean square of column 3 designated residual represents the variance within samplers. The F value of column 5 represents the ratio of the variance of the sample means to the variance of all samples. The last column presents the results of the ANOVA with respect to the null hypothesis. If the calculated F value is less than the "critical" F value (2.23 for 90% confidence; 3 degrees of freedom in means; 40 to 50 degrees of freedom in samples; F = 2.84 for 95% confidence), then there is a greater variation between samples than samplers. Table 10 (last column) indicates that the behavior of phenanthrene, benzo[a]pyrene, and PCB congeners 138 and 180 suggest a statistically significant difference in the four samplers. For phenanthrene, the difference is attributed to the

FIGURE 20.

Temporal Concentration Variations for Selected PCB Congeners Observed in the SM, RM, FM, and RA Samplers.

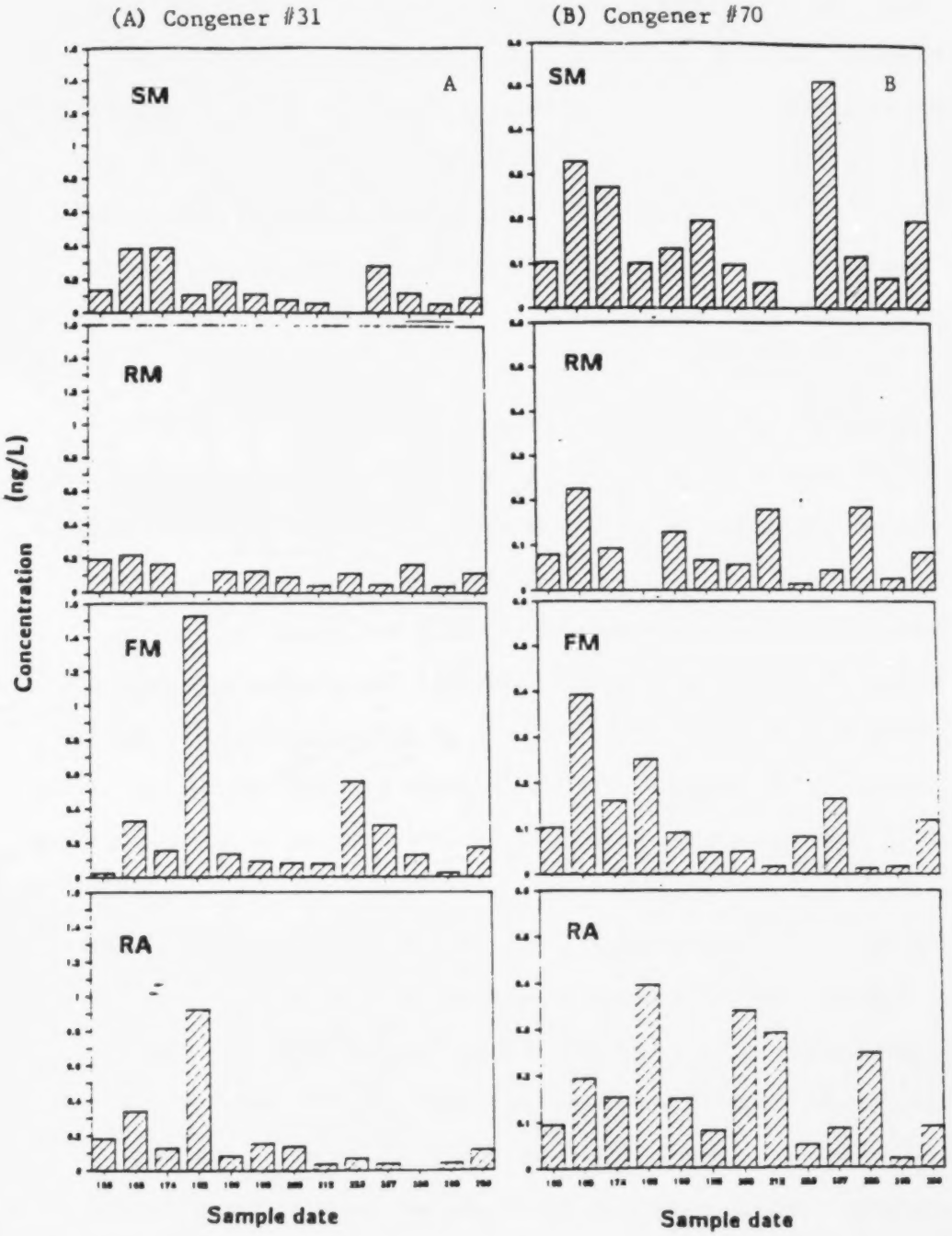


FIGURE 20.

Temporal Concentration Variations for Selected PCB Congeners Observed in the SM, RM, FM, and RA Samplers.

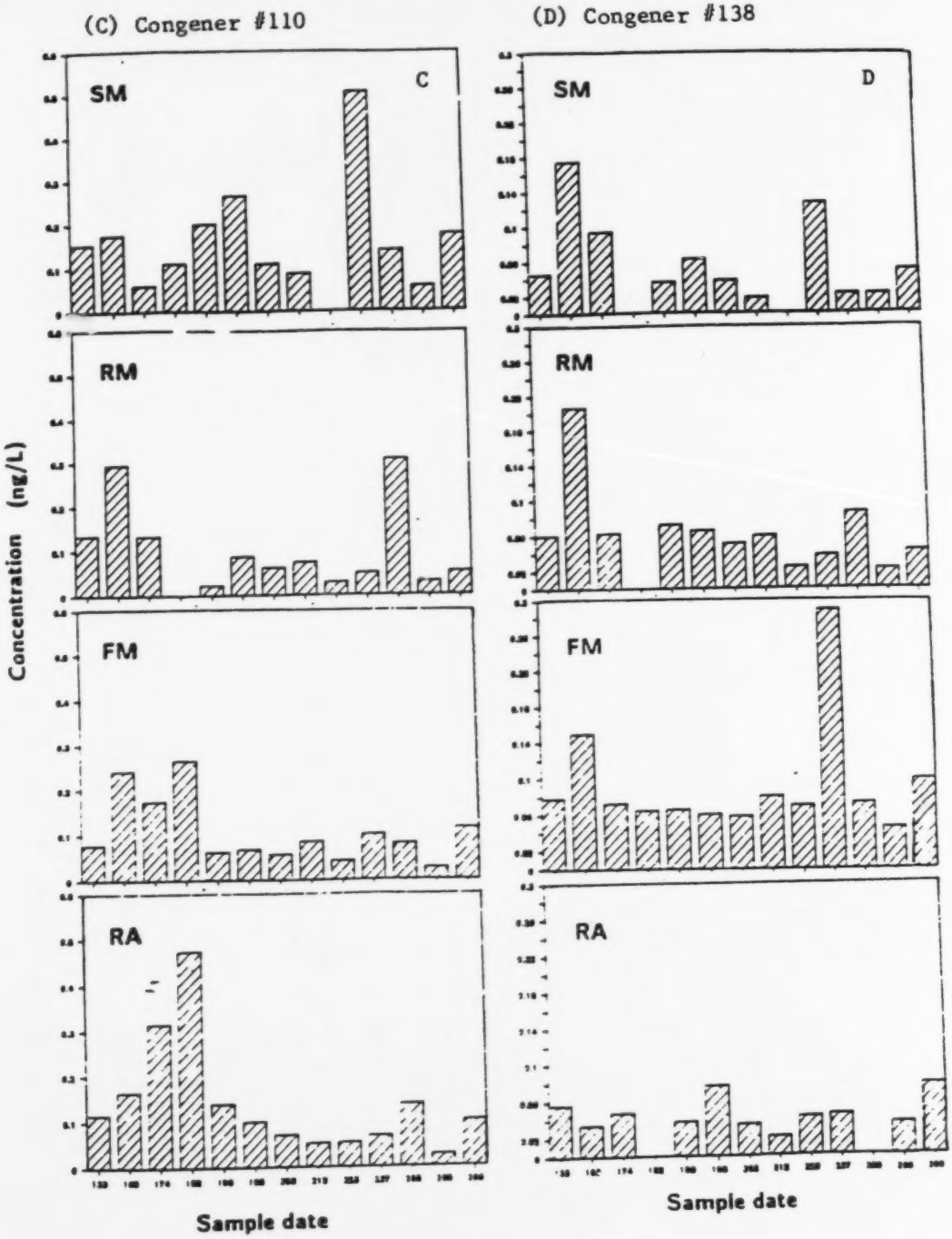


FIGURE 20.

Temporal Concentration Variations for Selected PCB Congeners Observed in the SM, RM, FM, and RA Samplers.

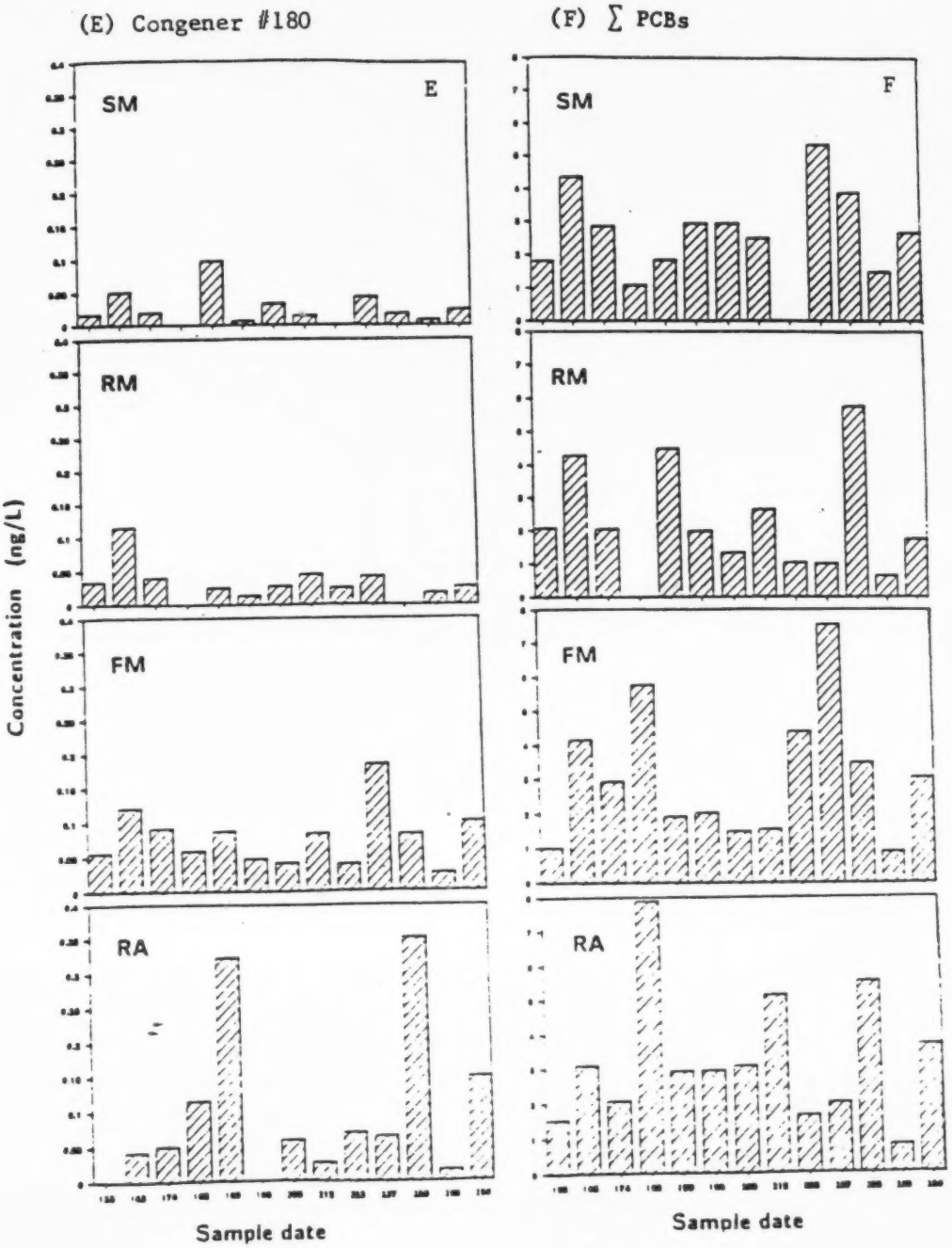


TABLE 10.

ANOVA Comparison of Fourteen Compounds in Four Precipitation Samplers

Compound	Mean Square Main Effect (Sampler)(a)	Degrees of Freedom	Residual(b)	Degrees of Freedom	"F" Value(c)	Difference between Samplers ? (d)
Phen	0.905	3	0.274	39	3.307	yes
Chr	1.236	3	2.415	39	0.512	no
B(a)P	6.983	3	1.185	39	5.895	yes
B(ghi)P	0.73	3	0.588	39	1.241	no
Total PAHs	0.323	3	0.527	39	0.614	no
HCB	0.955	3	1.127	38	0.847	no
p,p-DDE	3.199	3	1.882	38	1.7	no
Congener #31	0.26	3	0.759	45	0.342	no
Congener #70	1.603	3	0.742	46	2.159	no
Congener #110	0.854	3	0.528	46	1.617	no
Congener #138	0.959	3	0.315	43	3.049	yes
Congener #180	4.158	3	0.539	42	7.708	yes
Total PCBs	0.262	3	0.361	46	0.726	no
1,2,4-TCB	4.132	3	2.857	46	1.446	no

NOTES:

(a) Mean Square represents the variance between sampler means = (Var.0)^2 + 4(Var.1)^2, where (Var.1)^2 is the variance between samplers.

(b) Mean Square represents the variance within all samples = (Var.0)^2.

(c) "F" Value represents the ratio of the variance between the sampler means to the variance within all the samples.
For 90% Confidence interval the critical "F" value = 2.23
with 3 degrees of freedom in means and 40-50 degrees of freedom in samples.
For 95% Confidence interval the critical "F" value is 2.84 for
the same degrees of freedom.

(d) The null hypothesis is that there is no difference between samplers [(Var.1)^2 = 0].
which is true if calculated "F" value < critical "F" value.
This suggests that there is greater variation between samples than between samplers.
If the calculated "F" value > critical "F" value the null hypothesis is rejected,
which signifies that there is a difference between the samplers.

variations in the resin MIC sampler. For benzo[a]pyrene, the difference is attributed to variations in the SM sampler. The difference in collection behavior of PCB congeners is attributed to variations in the RA sampler. In general, these data support the null hypothesis that there is no or little significant difference in the collection efficiency of these 14 selected compounds. Where differences are significant, no consistent pattern emerges suggesting analytical causes may be responsible for some of the observed variation. The RA sampler has a collection surface area approximately 30% less than than the MIC samplers. Consequently less mass of compound was available for each sample potentially increasing the uncertainty of these measurements.

Sampling Protocols Affecting Collection of Organic Compounds

Interaction with Collection Surfaces

Falling rain comes into contact with the collection surfaces (i.e., funnels) and downstream parts of the sampling train. The funnels have coatings of either stainless steel (SM and RA samplers) or Teflon (RM and FM samplers). The sampling train consists of Teflon tubing and glass bottles (SM), glass reservoirs under the funnel followed by Teflon cartridges holding the XAD-2 resin (RM and RA) or an in-line filter holder and resin cartridge both made of Teflon (FM). Atmospheric particles scavenged from the atmosphere and organic vapors partitioned into the falling rain results in organic compounds being either associated with atmospheric particles or dissolved in aqueous solution. The particles may become attached to the collection surface and the dissolved species may be sorbed to the sampling train. To

evaluate this phenomenon, collection funnels and lower parts of the sampling train were rinsed with acetone or methanol following removal of the resin cartridges or rain bottles. For samples collected early in the 1986 field season, funnel rinses were analyzed separately. For the remaining field season, funnel rinses were combined with the resin or rain water extract.

Surprisingly, a significant if not dominant fraction of the total sample mass occurred in the funnel rinses irrespective of sampler and organic compound. Figure 21 presents a plot of the percentage of total sample mass occurring in the rinse for the fourteen selected compounds and four samplers. Table 11 presents the mean percentage of total sample mass occurring in the rinse for all organic compounds analyzed.

Table 11

Percentage of Compound Mass in Funnel Rinse

Sampler	PAHs	PCB Congeners	$\sum$ PCBs	Cl-Pesticides	Cl-Benzenes
SM	26	8-63	26	17	25
RM	27	22-72	62	21	32
FM	24	12-47	28	20	19
RA	28	13-77	37	15	31
All Samplers	26	23-55	40	18	28

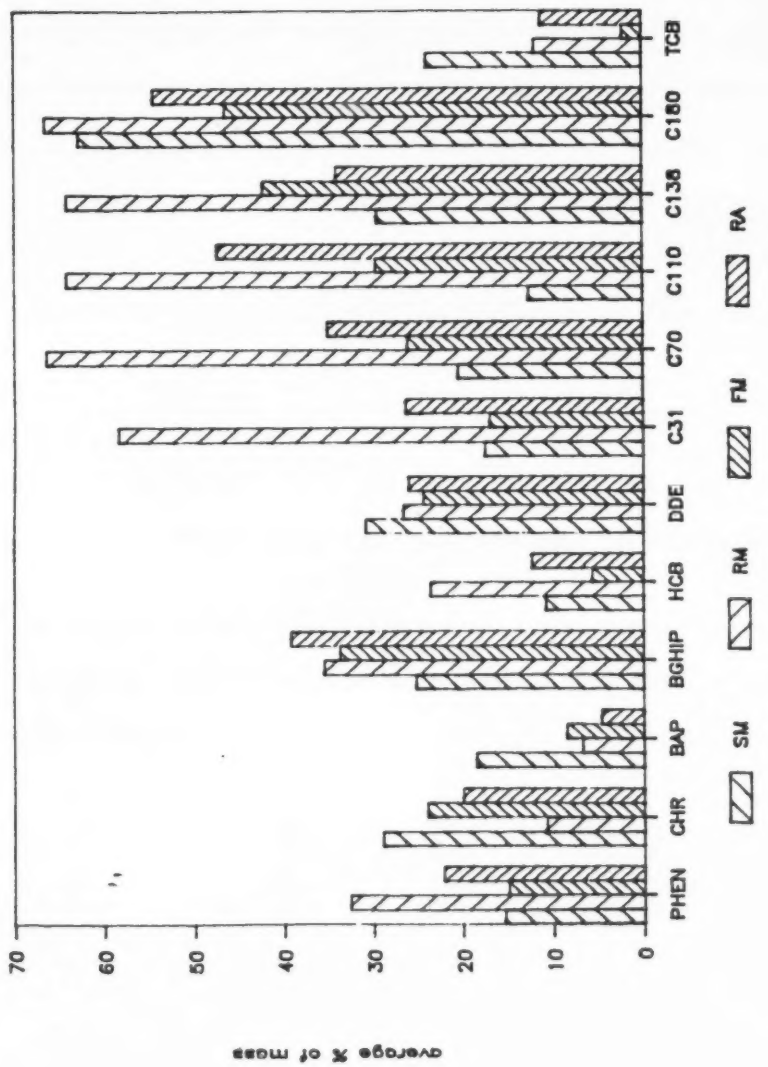


Figure 21. Percentage of 14 Selected PAHs and Chlorinated Hydrocarbons in the Funnel Rinse for the SM, RM, FM and RA Samplers

The PAHs exhibit a constant fraction of total sample mass, 26%, in the funnel rinse whereas PCBs exhibit widely varying amounts. The Cl-pesticides and Cl-benzenes also show a relatively constant fraction of their total sample mass to be in the rinse fraction. In all cases, a large percentage of the total sample mass occurs in the rinse independent of sampler, composition of funnel surface and specific compound. The RM sampler shows PCB congeners to be highly concentrated in the rinse of its sample train. The RM sampler has a Teflon collection surface and a 2 L glass reservoir in the sample train. The FM sampler is nearly identical except it has no glass reservoir. By intercomparison of the sampler behavior and sampler characteristics, the funnel contributes on average about 50% of the total mass in the rinse and the glass reservoir the other 50%.

This phenomenon is further examined in Figure 22 which shows the percentage of total sample mass in the rinse for PAHs (Figure 22A) and PCB congeners (Figure 22B). The retention of PAH in the RM sampler ranges from 10 to 50% and is independent of whether the compound is thought to be dissolved (e.g., phenanthrene) or particulate (e.g., B[a]pyrene. The pattern of retention is more pronounced for the PCBs. Figure 22B shows that nearly all PCB congeners are retained to some extent with some approaching 100% retention in the funnel and glass reservoir.

The problems associated with the retention of organic compounds in the funnel and sampling train may be easily solved by carefully rinsing the surfaces with the appropriate wetting solvent. These rinses may then be combined with the sample extract to yield an

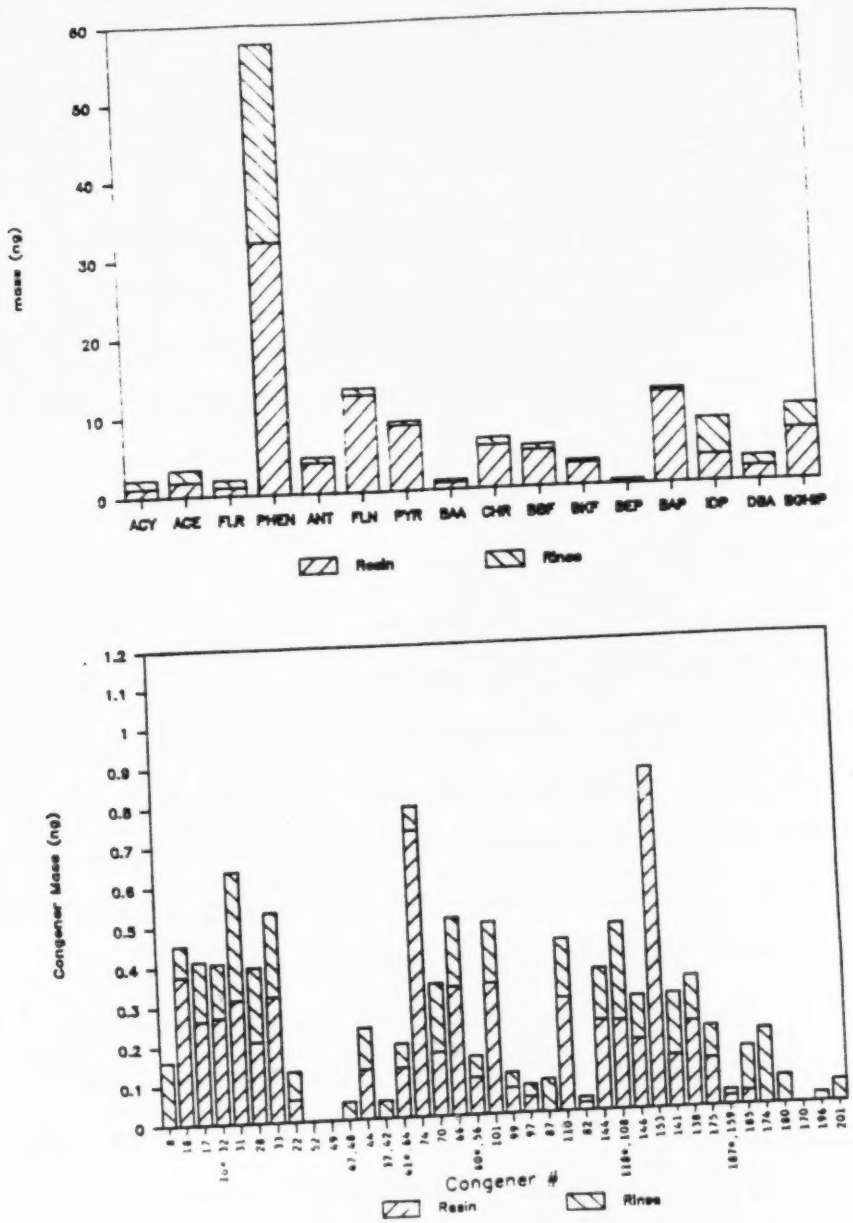


Figure 22. Percentage of (A) 17 PAHs and (B) 38 PCB Congeners in the Funnel Rinse of the RM Sampler on Julian Date 195, 1986

accurate assessment of the concentration. However, the problem does have significant implications with respect to quantifying atmospheric removal processes. It will be impossible to determine either the speciation of the organic compound in the collected rain or the form of the compound in the atmosphere. No information may be extracted on the mechanism with which particulate and gaseous species are removed by rain. The mechanistic information cannot be obtained using wet-only, integrating samplers. This type of information can only be confidently obtained using event, wet-only samplers such as the Pankow rain collector (Pankow et al., 1984) and taking special care to use and monitor inert surfaces.

Efficiency of the Solvent MIC Sampler

The solvent MIC (or SM) sampler isolates the organic compounds in rain using passive solvent extraction. The SM sampler has a Teflon tube running from the funnel to the bottom of a sampling bottle. The tube extends into a 200 mL layer of DCM which serves to isolate and preserve organics. The efficiency of this procedure was tested by collecting the contents of the first bottle and the contents of the reserve bottle and analyzing them separately for the first part of the 1986 study period. Figure 23 shows the fraction of the total mass of each of 17 PAHs and numerous PCB congeners in each bottle for one date. In general, the high MW PAHs presumably on particles were effectively isolated by the first bottle. A lesser portion of the low MW PAHs were isolated in the first bottle. On the order of 20 to 80% of the PCB congeners were retained in the second bottle with the lower MW species being least retained in the first bottle. Since DCM is

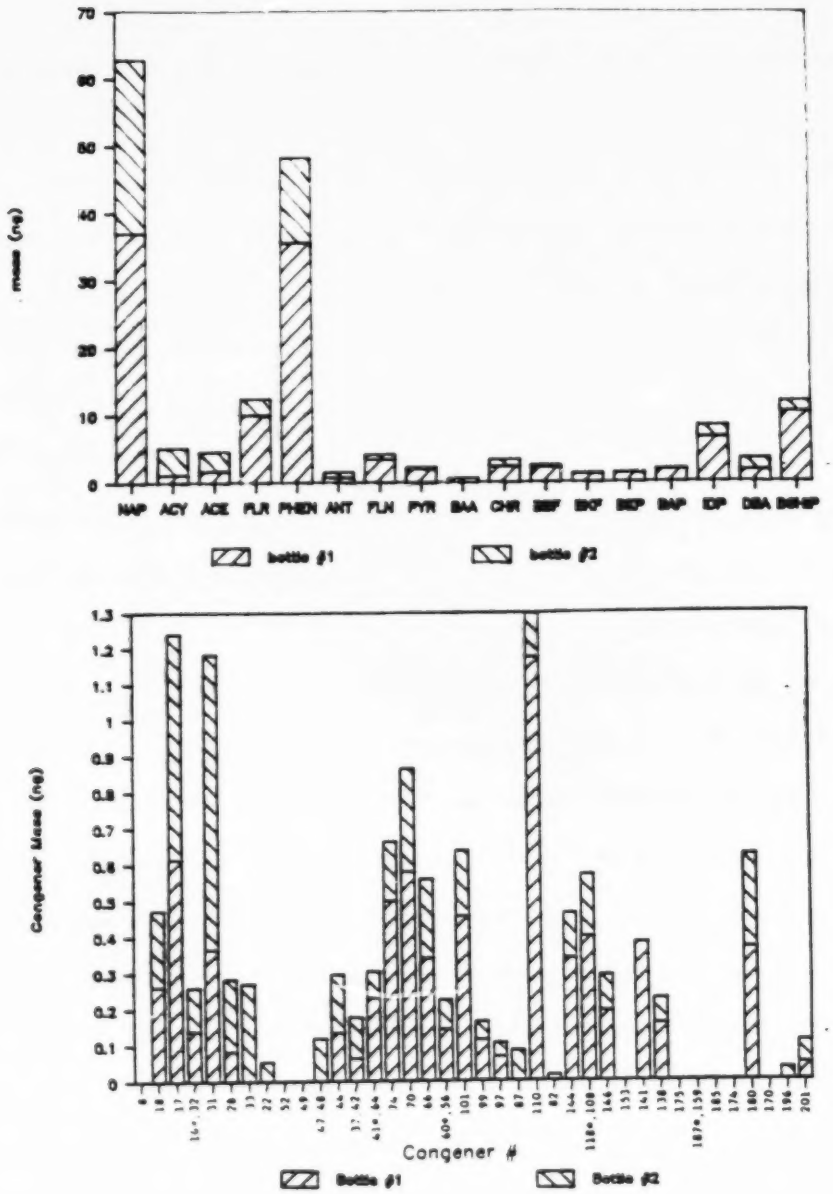

mass (ng)
NAP ACY ACE FLR PHEN ANT FLN PYR BAA CHR BBF BKF BEP BAP IDP DBA BGHIP
bottle #1
bottle #2
Congener Mass (ng)
Congener #
Bottle #1
Bottle #2

Figure 23. Percentage of (A) 17 PAHs and (B) 38 PCB Congeners in the 1st and 2nd Bottles of the SM Sampler on Julian Date 190, 1986

soluble to the extent of 1.5% in water, some of the organic compounds may have been solubilized and been transported into the second bottle. Equally likely is that simple passage of the rain through the DCM may not have been efficient. A solution to this problem is to place a mixer in the bottom of the first bottle which is activated by the moisture sensor. A larger water storage system is also needed to a volume of 20 L.

Separation of Particulate and Dissolved Species

The FM sampler is equipped with a Teflon-coated collection surface and an in-line filter assembly upstream of a Teflon cartridge containing XAD-2 resin. The filter is used to separate the particulate from the dissolved species so as to prevent resin clogging, enhance collection of particulate organic species and to provide data on atmospheric removal processes. As stated previously, the collection funnel retains a significant portion of the total sample mass of nearly all compounds tested and samplers tested. Since both dissolved and particulate species seem to be retained to variable degrees, it is unlikely that use of a filter is effective at establishing speciation. Figure 24 shows the percentage of the total mass of 17 PAHs and 38 PCB congeners in the filter, rinse and resin fractions for a single sample collected by the FM sampler. Of the total mass collected, approximately 10 to 30% of individual PAHs and PCBs were isolated on the filter. Table 12 provides a summary for all data collected.

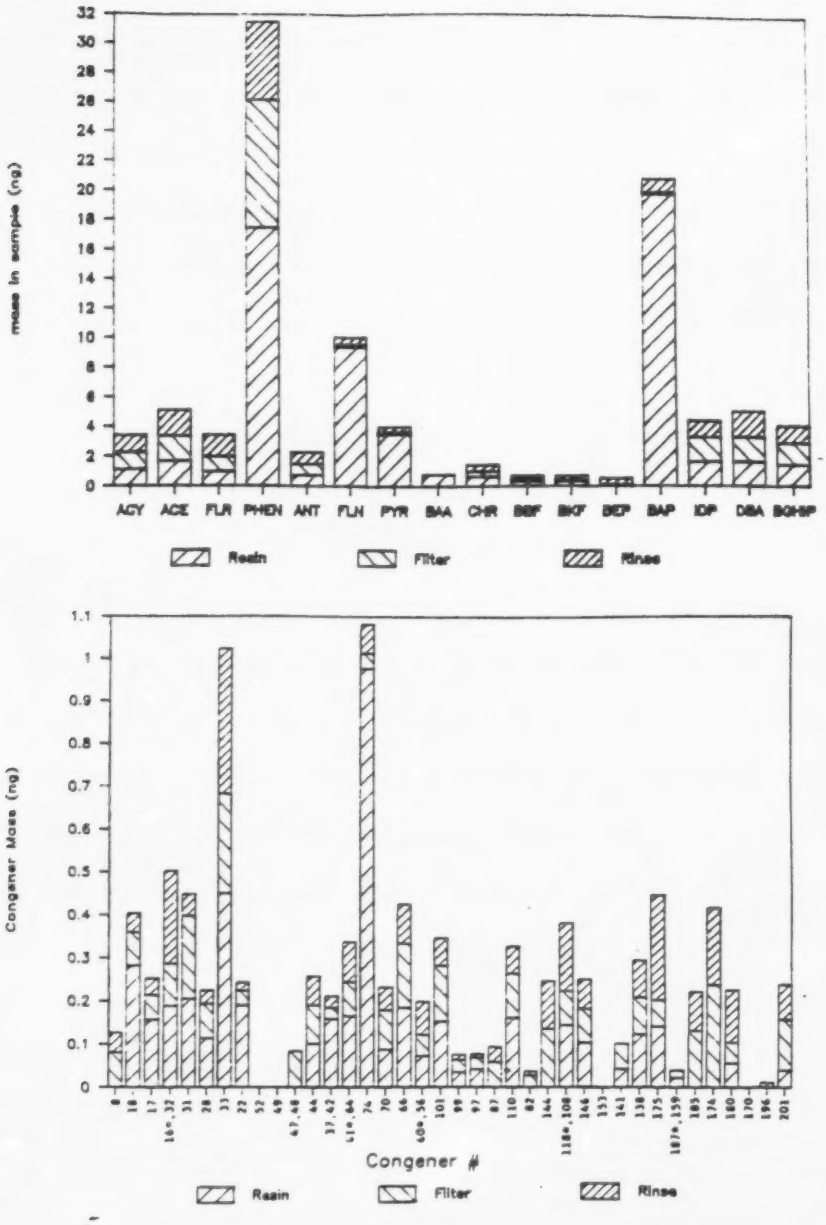


Figure 24. Percentage of (A) 17 PAHs and (B) 38 PCB Congeners in the Resin Adsorbent, Filter and Funnel Rinse of the FM Sampler on Julian Date 195, 1986

Table 12

Percentage of Total Compound Mass on the Filter

Sampler	PAHs	PCB Congeners	∑ PCBs	Cl-Pesticides	Cl-Benzenes
FM	30	9-67	29	18	27

One problem observed with this sampler in this study and also by Maris Lucis is that the filter clogs when large quantities of soil dust or pollen are scavenged from the atmosphere. In those instances, rain water is trapped in the funnel. A solution to this problem is to install an in-line peristaltic pump to assist in water passage through the sampling train and to use a pre-filter. However it is not clear whether filters can provide useful information in integrating samplers.

Mechanical Reliability and Operational Characteristics

MECHANICAL RELIABILITY AND OPERATIONAL CHARACTERISTICS

In a monitoring network, a wet-only, integrating sampler must be able to reliably operate unattended for periods of approximately two weeks. All of the samplers demonstrated this ability or have the potential to do so with proper maintenance, careful operation, or with minor design modifications. During the course of this study, a variety of problems were encountered which could adversely effect sample quality. Table 13 lists the problems that occurred with each sampler

Table 13

Problems in field operation

date	SM	RM	FM	RA
133	O			
163	C	F,C	F	
174	O		F	
182				?
190				
195			F	S
203				
212		C	F	R
223			F	R
237		R	X	
255	O		F	
265	O	R	F,C,X	R
286		R	R,C	

C: cover open on arrival
F: standing water in funnel
O: overflow of collection bottles
R: standing water in reservior
S: moisture sensor malfunction
X: blown fuse
?: carboy empty, cause unknown

by sampling date.

The MIC samplers exhibited the greater number of mechanical difficulties. A funnel cover was found open on five occasions due to a loose cotter pin (RM) or allen bolt (SM) on the motor shaft sprocket, and twice a fuse blew (FM). This would allow dry deposition to be incorporated into the sample. Conversely, no sample would be collected if the cover failed to open, which did occur once. These malfunctions are symptoms of the basic weakness of the MIC sampler; namely, the mechanism of opening and closing the cover does not seem designed to sustain the generated torque. The Aerochem Metrics sampler, which has a weighted counterbalance for its cover, never exhibited this type of mechanical failure. The only mechanical problem observed with the RA sampler involved the moisture sensor, which became either insensitive or slow to respond and was replaced.

Operational difficulties encountered could not be differentiated according to manufacturer's design, but varied according to mode of isolation: resin adsorption or solvent extraction. Since gravity flow through the resin was approximately 40 mL/min, water would accumulate in the reservoir or collection funnel during periods of intense or prolonged rainfall. Standing water could allow volatilization to occur prior to resin isolation, and enhance the possibility of adsorption to sampling train surfaces. Debris such as leaf material or insects occasionally clogged the fittings on the resin samplers and restricted flow. The RA sampler exhibited few operational problems of this sort due to the smaller volumes collected.

Due to its design, the SM sampler did not experience any flow restriction. However, since the sampling bottles have a bulk water capacity of 8 L, overflow, probable loss of contaminant mass, and inaccurate volume measurement occurred on four occasions when rainfall exceeded 1.5 inches (3.9 cm). This diminished its ability to remain unattended during especially wet periods of the year. In addition, the lack of effective passive extraction by the solvent in the primary sample bottle contributed to contaminant loss with overflow. A deeper solvent layer with active stirring or agitation to enhance the contact between solvent and water, and a larger volume capacity would increase the efficiency of the extraction process and decrease overflow losses. The headspace above the water in the sample bottles could lead to evaporative losses or air/water exchange, although the pinch clamp attempts to close the system to the atmosphere. The weight and bulk of the sample bottles and presence of solvent could present transportation problems and higher shipping costs in an extensive monitoring network. Mechanically, the allen bolt on the motor shaft sprocket and the clutch plate would loosen and required tightening with each sampling visit. The advantages of the SM sampler include the sampling train design that prevents flow restriction, contains less surface for adsorption, and allows particles to be incorporated into the sample. The sampler, which is heated and insulated, is suitable for all-weather operation. Finally, the MIC sensor appeared to be superior in its sensitivity and response to precipitation.

The RM sampler suffered mechanical problems similar to the SM. In this case, a cotter pin holding the sprocket to the motor shaft, a modification to solve the allen bolt problem of the SM, was periodically sheared off. Flow restriction due to the resin and occasional plugs of insect or plant material caused water to back-up into the reservoir or funnel. Material did adhere to the surface of the glass reservoir but it was assumed that by rinsing the sampling train with solvent the adsorbed organics were extracted. Resin adsorption of particulate organics is questionable, since discolored glass wool plugs at each end of the resin cartridge were noted and suggested particle breakthrough. The beneficial characteristics of the RM sampler include the large 20 L capacity; the MIC moisture sensor; the lightweight and easily transported XAD-2 resin adsorption system; and the aluminum foil covered reservoir, which serves to protect compounds from photolysis and limit evaporative losses prior to resin extraction.

The FM sampler did not exhibit any motor sprocket problems. However, fuses did periodically need replacement which suggested a short or strain on the electical system. The characteristics of the FM are similar to the RM, except that it had an in-line filter and was without a reservoir. The major problem encountered was associated with the filter. During seven of the thirteen sampling periods, the FM sampler had standing water in the funnel attributable to either plugged filter pores or insufficient head pressure for proper flow. A peristaltic pump activated by the moisture sensor or a volumetric sensor would alleviate this problem.

The RA sampler was the most mechanically reliable sampler evaluated. The counterbalanced cover prevented the strain that contributed to the MIC malfunctions. Disadvantages of the RA include the moisture sensor, which did not seem as sensitive or responsive as the MIC sensor, and the small funnel surface area. The collection of less volume and contaminant mass can influence the detectability of some trace organics. Since the sampling train was similar to the RM, the problems and advantages discussed above also apply to the RA.

CONCLUSIONS

Four wet-only precipitation samplers were deployed at a site near Minneapolis, MN in 1986 with the objective of comparing the ability of each to provide precise estimates of trace organic concentrations and fluxes in rain. The four samplers were evaluated and compared on the basis of their ability to efficiently collect rainfall, exhibit mechanical reliability, demonstrate adequate operational characteristics and precise measures of wet-only inputs. The samplers differed in collection surface area, type of collection surface, mode of organic compound isolation and operational characteristics. The samplers consisted of modified MIC rain collectors (Meterological Instruments Co.) and a modified Aerochem Metrics collector.

The overall conclusion of this study is that the four samplers collected rain volumes and a mixture of chlorinated hydrocarbons and polycyclic aromatic hydrocarbons equally well. The overall performance of the samplers was more closely linked to mechanical and operational characteristics than to ability to precisely assess wet-only concentrations of organic compounds in rain.

The four samplers all collected 95% of rain gauge volume when functioning properly. Mechanical malfunctions (blown fuses, loose bolts, stuck arms) reduced rain collection efficiency to 82 to 90%.

Volume-weighted mean concentrations of 14 selected organic compounds generally agreed within statistical propagated error limits. One-way ANOVA comparison of the samplers using log-normalized concentration data generally showed no difference in individual sampler performance.

One characteristic exhibited by all samplers was the occurrence of a significant (if not dominant) fraction of the total sample mass in the solvent rinse of the funnel. This behavior occurred in all samplers independent of whether the surface was stainless steel or Teflon, but was exacerbated by use of a glass reservior. Attention to this detail in the sampling protocol is important in assessing rain concentrations. However this phenomenon makes determination of atmospheric removal processes and compound speciation all but impossible.

The MIC sampler, having a surface area of 0.2 m^2, is an appropriate collector for unattended operation (2 weeks) in a monitoring network. The use of XAD-2 resin cartridge or batch solvent

extraction is adequate for characterizing concentrations of organic compounds in rain. The former exhibits higher blanks but has the advantage of in-situ isolation in the field. The MIC-solvent combination requires incorporation of an active mixing process to be more effective.

Although this project did not have as its objective to determine the uncertainty in flux measurements, the propagated error within samplers suggests that loading estimates of organic contaminants at trace concentrations can be no less than ± 20%.

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APPENDIX A
PAH CONCENTRATIONS IN RAIN - 1986

PAH concentrations in Precipitation-1986
(ng/L)

--naphthalene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	10.2	10.9	6.7	3.1	26.8	12
Resin MIC						
Filter MIC						
Resin Aerochem						
all samplers	10.2	10.9	6.7	3.1	26.8	12

--acenaphthylene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.1	1.0	0.7	0.1	2.1	12
Resin MIC	0.9	1.0	1.6	0.1	5.6	10
Filter MIC	1.9	1.9	1.4	0.5	4.8	10
Resin Aerochem	1.8	1.3	1.3	0.3	4.9	10
all samplers	1.3	1.3	1.3	0.1	5.6	42

--acenaphthene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.7	0.7	0.5	0.2	1.6	12
Resin MIC	2.1	2.6	2.3	0.3	8.2	10
Filter MIC	0.7	0.8	0.4	0.3	1.9	10
Resin Aerochem	2.9	2.3	1.7	0.5	5.5	10
all samplers	1.3	1.6	1.7	0.2	8.2	42

--fluorene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.8	1.9	1.1	0.3	4.1	13
Resin MIC	1.6	2.0	1.5	0.3	4.5	10
Filter MIC	1.1	1.2	0.8	0.6	3.1	10
Resin Aerochem	1.2	1.5	1.0	0.3	2.9	10
all samplers	1.5	1.7	1.1	0.3	4.5	43

--phenanthrene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	8.6	9.1	4.2	2.2	17.7	13
Resin MIC	15.3	19.6	16.5	5.1	62.8	10
Filter MIC	8.8	8.9	2.9	4.9	15.1	10
Resin Aerochem	11.2	12.4	3.7	6.0	18.8	10
all samplers	10.6	12.3	9.6	2.2	62.8	43

--anthracene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.2	0.3	0.2	.0	0.9	13
Resin MIC	0.3	0.3	0.3	.0	0.9	10
Filter MIC	0.3	0.3	0.2	0.1	0.6	10
Resin Aerochem	0.3	0.4	0.2	0.1	0.8	10
all samplers	0.3	0.3	0.2	.0	0.9	43

--fluoranthene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	7.9	7.9	9.9	0.2	32.5	13
Resin MIC	10.1	10.5	9.9	0.4	36.4	10
Filter MIC	7.8	7.0	5.9	0.5	18.5	10
Resin Aerochem	8.5	8.3	7.2	0.6	24.7	10
all samplers	8.5	8.4	8.6	0.2	36.4	43

--pyrene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	5.2	5.3	7.1	0.1	25.0	13
Resin MIC	7.3	7.7	7.9	0.3	28.7	10
Filter MIC	5.8	5.2	4.5	0.3	14.0	10
Resin Aerochem	7.5	7.1	5.9	0.6	19.8	10
all samplers	6.1	6.2	6.6	0.1	28.7	43

--benzo[a]anthracene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	2.4	2.6	2.8	.0	7.6	11
Resin MIC	3.7	4.3	4.4	0.2	14.9	8
Filter MIC	3.1	2.9	2.5	0.2	7.1	8
Resin Aerochem	3.1	3.1	2.6	0.2	8.6	8
all samplers	3.0	3.2	3.2	.0	14.9	35

--chrysene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	6.1	6.7	8.4	0.2	27.4	13
Resin MIC	6.5	7.0	6.9	0.3	23.4	10
Filter MIC	5.1	4.5	4.7	0.3	14.9	10
Resin Aerochem	5.6	5.3	5.0	0.4	15.5	10
all samplers	5.9	5.9	6.7	0.2	27.4	43

--benzo[b]fluoranthene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.8	1.9	1.9	0.2	5.1	13
Resin MIC	2.3	2.4	2.2	0.2	8.0	10
Filter MIC	1.6	1.5	1.5	0.1	4.9	10
Resin Aerochem	1.9	1.9	1.9	0.1	6.8	10
all samplers	1.9	1.9	1.9	0.1	8.0	43

--benzo[k]fluoranthene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.3	1.4	1.6	0.1	4.2	13
Resin MIC	1.6	1.7	1.6	0.1	5.4	10
Filter MIC	1.3	1.2	1.3	0.1	4.4	10
Resin Aerochem	1.5	1.5	1.2	0.1	4.1	10
all samplers	1.4	1.4	1.5	0.1	5.4	43

--benz[e]pyrene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.2	1.3	1.4	0.1	3.7	12
Resin MIC	1.7	1.9	1.7	0.1	5.8	8
Filter MIC	1.5	1.4	1.1	0.2	3.3	8
Resin Aerochem	1.7	1.7	1.4	0.1	4.3	8
all samplers	1.4	1.5	1.4	0.1	5.8	36

--benzo[a]pyrene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.4	1.5	1.7	0.1	4.7	13
Resin MIC	3.3	3.5	2.6	0.4	9.4	10
Filter MIC	2.9	3.0	1.8	0.7	6.4	10
Resin Aerochem	3.5	3.8	2.1	0.9	7.0	10
all samplers	2.5	2.9	2.2	0.1	9.4	43

--idene[123-c,d]pyrene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	2.0	2.2	1.3	0.7	5.3	13
Resin MIC	2.0	2.1	2.1	0.3	6.9	10
Filter MIC	1.4	1.4	0.9	0.2	3.0	10
Resin Aerochem	2.1	2.2	1.5	0.5	5.8	10
all samplers	1.8	2.0	1.6	0.2	6.9	43

--dibenzo[a,h]anthracene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.5	0.5	0.4	0.2	1.8	13
Resin MIC	0.7	0.8	0.9	0.1	3.3	10
Filter MIC	0.5	0.6	0.3	0.2	1.1	10
Resin Aerochem	0.7	0.9	0.5	0.2	1.7	10
all samplers	0.6	0.7	0.6	0.1	3.3	43

--benzo[g,h,i]perylene--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	2.2	2.3	1.1	0.4	4.9	13
Resin MIC	1.9	2.1	2.1	0.3	8.1	10
Filter MIC	1.4	1.4	0.9	0.2	3.5	10
Resin Aerochem	1.5	1.7	1.1	0.4	3.9	10
all samplers	1.9	1.9	1.4	0.2	8.1	43

--total PAH--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	53.9	56.0	41.7	9.7	130.7	13
Resin MIC	60.5	68.3	49.9	13.6	198.6	10
Filter MIC	44.4	42.3	27.4	15.0	98.9	10
Resin Aerochem	54.2	54.3	31.2	22.9	121.3	10
all samplers	53.0	55.3	39.8	9.7	198.6	43

APPENDIX B
PCB CONCENTRATIONS IN RAIN - 1986

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 8 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.002	0.045		0.05	0.05	1
Resin MIC	0.072	0.098	0.12	0.02	0.42	9
Filter MIC	0.052	0.082	0.07	0.03	0.23	9
Resin Aerochem	0.162	0.281	0.58	0.02	1.69	7
All Samplers	0.057	0.140	0.32	0.02	1.69	26

I.U.P.A.C. # -- Congener 18 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.06	0.07	0.04	0.02	0.17	12
Resin MIC	0.11	0.12	0.13	0.02	0.52	12
Filter MIC	0.12	0.14	0.08	0.03	0.36	12
Resin Aerochem	0.20	0.25	0.26	0.04	1.07	12
All Samplers	0.11	0.14	0.17	0.02	1.07	48

I.U.P.A.C. # -- Congener 17 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.20	0.19	0.09	0.053	0.33	12
Resin MIC	0.17	0.16	0.14	0.007	0.44	12
Filter MIC	0.09	0.13	0.12	0.007	0.41	12
Resin Aerochem	0.15	0.15	0.15	0.009	0.53	13
All Samplers	0.15	0.16	0.13	0.007	0.53	49

I.U.P.A.C. # -- Congener 16*,32 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.038	0.04	0.02	0.016	0.08	12
Resin MIC	0.077	0.09	0.15	0.011	0.58	12
Filter MIC	0.067	0.09	0.07	0.008	0.24	12
Resin Aerochem	0.052	0.08	0.06	0.015	0.24	12
All Samplers	0.060	0.07	0.09	0.008	0.58	48

I.U.P.A.C. # -- Congener 31 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.16	0.17	0.11	0.056	0.39	12
Resin MIC	0.12	0.12	0.06	0.038	0.22	12
Filter MIC	0.19	0.28	0.39	0.024	1.53	13
Resin Aerochem	0.13	0.19	0.24	0.038	0.93	12
All Samplers	0.15	0.19	0.25	0.024	1.53	49

I.U.P.A.C. # -- Congener 28 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.08	0.09	0.09	0.013	0.31	11
Resin MIC	0.06	0.07	0.05	0.019	0.21	12
Filter MIC	0.10	0.13	0.16	0.004	0.62	13
Resin Aerochem	0.07	0.11	0.11	0.015	0.37	12
All Samplers	0.08	0.10	0.12	0.004	0.62	48

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 33 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.49	0.75	0.81	0.014	2.18	8
Resin MIC	0.10	0.12	0.07	0.063	0.30	11
Filter MIC	0.26	0.28	0.37	0.01	1.43	13
Resin Aerochem	0.14	0.21	0.08	0.101	0.37	10
All Samplers	0.27	0.31	0.47	0.01	2.18	42

I.U.P.A.C. # -- Congener 22 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.019	0.04	0.06	0.002	0.18	7
Resin MIC	0.024	0.03	0.02	0.007	0.08	11
Filter MIC	0.068	0.10	0.15	0.004	0.47	10
Resin Aerochem	0.052	0.07	0.16	0.004	0.51	9
All Samplers	0.039	0.06	0.12	0.002	0.51	37

I.U.P.A.C. # -- Congener 52 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.027	0.14		0.144	0.14	1
Resin MIC	0.031	0.20	0.14	0.065	0.34	2
Filter MIC	0.098	0.32	0.17	0.112	0.55	4
Resin Aerochem	0.085	0.96		0.961	0.96	1
All Samplers	0.057	0.35	0.28	0.065	0.96	8

I.U.P.A.C. # -- Congener 49 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.009	0.032	0.020	0.010	0.06	4
Resin MIC	0.004	0.016	0.007	0.007	0.02	3
Filter MIC	0.051	0.197	0.200	0.023	0.48	3
Resin Aerochem	0.016	0.093	0.078	0.015	0.17	2
All Samplers	0.021	0.079	0.128	0.007	0.48	12

I.U.P.A.C. # -- Congener 47*,48 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.021	0.040	0.041	0.009	0.14	8
Resin MIC	0.014	0.038	0.054	0.008	0.15	5
Filter MIC	0.059	0.092	0.107	0.012	0.33	8
Resin Aerochem	0.067	0.201	0.256	0.023	0.64	4
All Samplers	0.036	0.082	0.136	0.008	0.64	25

I.U.P.A.C. # -- Congener 44 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.055	0.067	0.050	0.023	0.22	11
Resin MIC	0.030	0.037	0.026	0.014	0.11	11
Filter MIC	0.114	0.138	0.243	0.012	0.95	13
Resin Aerochem	0.052	0.073	0.060	0.0[illegible]	0.25	12
All Samplers	0.065	0.081	0.140	0.0[illegible]	0.95	47

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 37,42 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.018	0.029	0.028	0.011	0.11	9
Resin MIC	0.025	0.029	0.031	0.009	0.12	10
Filter MIC	0.073	0.099	0.145	0.011	0.54	11
Resin Aerochem	0.046	0.072	0.042	0.021	0.17	10
All Samplers	0.040	0.059	0.087	0.009	0.54	40

I.U.P.A.C. # -- Congener 41,64 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.07	0.08	0.04	0.013	0.17	11
Resin MIC	0.04	0.05	0.02	0.013	0.09	12
Filter MIC	0.09	0.11	0.08	0.012	0.28	12
Resin Aerochem	0.13	0.18	0.20	0.02	0.68	12
All Samplers	0.07	0.11	0.12	0.012	0.68	47

I.U.P.A.C. # -- Congener 74 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.13	0.24	0.24	0.024	0.72	8
Resin MIC	0.10	0.15	0.17	0.009	0.51	9
Filter MIC	0.07	0.08	0.09	0.006	0.29	13
Resin Aerochem	0.12	0.17	0.11	0.04	0.33	10
All Samplers	0.10	0.15	0.16	0.006	0.72	40

I.U.P.A.C. # -- Congener 70 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.16	0.18	0.13	0.059	0.52	12
Resin MIC	0.09	0.10	0.07	0.014	0.23	12
Filter MIC	0.09	0.12	0.10	0.013	0.39	13
Resin Aerochem	0.14	0.17	0.11	0.021	0.40	13
All Samplers	0.12	0.14	0.11	0.013	0.52	50

I.U.P.A.C. # -- Congener 66 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.17	0.18	0.13	0.058	0.46	12
Resin MIC	0.12	0.12	0.13	0.021	0.51	12
Filter MIC	0.14	0.17	0.13	0.020	0.37	13
Resin Aerochem	0.15	0.20	0.13	0.042	0.45	12
All Samplers	0.14	0.17	0.13	0.020	0.51	49

I.U.P.A.C. # -- Congener 60*,56 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.043	0.050	0.042	0.016	0.17	12
Resin MIC	0.034	0.035	0.027	0.012	0.11	12
Filter MIC	0.053	0.063	0.042	0.006	0.16	13
Resin Aerochem	0.051	0.065	0.053	0.014	0.22	13
All Samplers	0.044	0.053	0.044	0.006	0.22	50

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 101 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.19	0.22	0.15	0.077	0.54	12
Resin MIC	0.10	0.10	0.05	0.041	0.21	12
Filter MIC	0.10	0.12	0.08	0.022	0.29	13
Resin Aerochem	0.12	0.15	0.14	0.037	0.60	13
All Samplers	0.13	0.15	0.12	0.022	0.60	50

I.U.P.A.C. # -- Congener 99 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.042	0.057	0.038	0.015	0.13	10
Resin MIC	0.037	0.040	0.051	0.009	0.19	12
Filter MIC	0.020	0.025	0.020	0.003	0.08	11
Resin Aerochem	0.100	0.132	0.293	0.007	0.96	9
All Samplers	0.041	0.060	0.145	0.003	0.96	42

I.U.P.A.C. # -- Congener 97 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.028	0.034	0.023	0.007	0.08	11
Resin MIC	0.016	0.023	0.018	0.003	0.06	9
Filter MIC	0.008	0.011	0.006	0.002	0.02	10
Resin Aerochem	0.047	0.064	0.076	0.008	0.23	11
All Samplers	0.021	0.034	0.046	0.002	0.23	41

I.U.P.A.C. # -- Congener 87 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.046	0.051	0.035	0.013	0.15	12
Resin MIC	0.013	0.027	0.019	0.014	0.07	7
Filter MIC	0.007	0.016	0.011	0.005	0.04	8
Resin Aerochem	0.010	0.039	0.009	0.027	0.05	4
All Samplers	0.021	0.035	0.028	0.005	0.15	31

I.U.P.A.C. # -- Congener 110 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.15	0.17	0.12	0.056	0.51	12
Resin MIC	0.11	0.11	0.09	0.023	0.31	12
Filter MIC	0.09	0.11	0.07	0.027	0.26	13
Resin Aerochem	0.11	0.14	0.12	0.026	0.47	13
All Samplers	0.11	0.13	0.11	0.023	0.51	50

I.U.P.A.C. # -- Congener 82 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.004	0.007	0.006	0.001	0.02	6
Resin MIC	0.009	0.009	0.007	0.003	0.03	12
Filter MIC	0.009	0.010	0.007	0.002	0.03	12
Resin Aerochem	0.013	0.025	0.034	0.002	0.12	10
All Samplers	0.008	0.013	0.020	0.001	0.12	40

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 144 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.045	0.059	0.043	0.019	0.163	10
Resin MIC	0.075	0.093	0.062	0.020	0.209	11
Filter MIC	0.085	0.090	0.055	0.023	0.218	13
Resin Aerochem	0.095	0.153	0.107	0.022	0.330	11
All Samplers	0.071	0.099	0.078	0.019	0.330	45

I.U.P.A.C. # -- Congener 118*,108 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.07	0.09	0.07	0.021	0.30	11
Resin MIC	0.20	0.27	0.33	0.040	1.07	9
Filter MIC	0.08	0.08	0.03	0.028	0.15	13
Resin Aerochem	0.07	0.10	0.07	0.036	0.26	9
All Samplers	0.11	0.13	0.18	0.021	1.07	42

I.U.P.A.C. # -- Congener 146 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.053	0.059	0.040	0.020	0.16	12
Resin MIC	0.048	0.057	0.029	0.020	0.13	11
Filter MIC	0.055	0.065	0.035	0.019	0.14	13
Resin Aerochem	0.038	0.054	0.023	0.017	0.09	11
All Samplers	0.050	0.059	0.033	0.017	0.16	47

I.U.P.A.C. # -- Congener 153 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.10	0.17	0.08	0.078	0.28	6
Resin MIC	0.18	0.36	0.41	0.077	1.34	7
Filter MIC	0.11	0.22	0.11	0.065	0.42	8
Resin Aerochem	0.11	0.34	0.13	0.173	0.49	5
All Samplers	0.13	0.27	0.24	0.065	1.34	26

I.U.P.A.C. # -- Congener 141 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.013	0.019	0.017	0.006	0.06	10
Resin MIC	0.017	0.027	0.025	0.004	0.08	10
Filter MIC	0.015	0.022	0.010	0.010	0.04	9
Resin Aerochem	0.014	0.036	0.018	0.011	0.07	6
All Samplers	0.015	0.025	0.019	0.004	0.08	35

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 138 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.053	0.062	0.047	0.017	0.17	11
Resin MIC	0.060	0.066	0.046	0.022	0.21	12
Filter MIC	0.088	0.093	0.062	0.046	0.29	13
Resin Aerochem	0.040	0.046	0.017	0.020	0.08	11
All Samplers	0.064	0.068	0.050	0.017	0.29	47

I.U.P.A.C. # -- Congener 175 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.026	0.051	0.040	0.012	0.11	7
Resin MIC	0.106	0.119	0.193	0.015	0.71	11
Filter MIC	0.038	0.051	0.024	0.012	0.09	9
Resin Aerochem	0.026	0.065	0.056	0.026	0.18	5
All Samplers	0.052	0.076	0.121	0.012	0.71	32

I.U.P.A.C. # -- Congener 187*,159 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.006	0.008	0.005	0.003	0.021	11
Resin MIC	0.010	0.015	0.018	0.004	0.062	8
Filter MIC	0.010	0.012	0.012	0.004	0.044	10
Resin Aerochem	0.009	0.018	0.008	0.004	0.027	7
All Samplers	0.009	0.013	0.012	0.003	0.062	36

I.U.P.A.C. # -- Congener 185 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.009	0.016	0.013	0.003	0.05	7
Resin MIC	0.014	0.024	0.020	0.006	0.07	8
Filter MIC	0.025	0.041	0.035	0.008	0.13	10
Resin Aerochem	0.021	0.043	0.036	0.005	0.13	9
All Samplers	0.016	0.032	0.031	0.003	0.13	34

I.U.P.A.C. # -- Congener 174 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.005	0.014	0.009	0.003	0.03	5
Resin MIC	0.007	0.021	0.016	0.006	0.04	5
Filter MIC	0.023	0.053	0.058	0.003	0.18	8
Resin Aerochem	0.028	0.147	0.192	0.025	0.53	5
All Samplers	0.014	0.058	0.108	0.003	0.53	23

Data Summary: PCBs - 1986 RAIN

I.U.P.A.C. # -- Congener 180 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.024	0.030	0.025	0.006	0.097	11
Resin MIC	0.031	0.038	0.026	0.014	0.116	11
Filter MIC	0.072	0.078	0.041	0.025	0.184	13
Resin Aerochem	0.083	0.116	0.111	0.016	0.352	11
All Samplers	0.048	0.066	0.070	0.006	0 352	46

I.U.P.A.C. # -- Congener 170 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.001	0.019		0.019	0.019	1
Resin MIC	0.002	0.018		0.018	0.018	1
Filter MIC	0.002	0.018	0.002	0.016	0.020	2
Resin Aerochem	0.002	0.066		0.066	0.066	1
All Samplers	0.002	0.028	0.019	0.016	0.066	5

I.U.P.A.C. # -- Congener 196 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.004	0.006	0.003	0.002	0.012	9
Resin MIC	0.005	0.006	0.004	0.002	0.015	9
Filter MIC	0.015	0.029	0.039	0.002	0.111	10
Resin Aerochem	0.017	0.057	0.101	0.002	0.304	7
All Samplers	0.009	0.023	0.054	0.002	0.304	35

I.U.P.A.C. # -- Congener 201 --

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	0.012	0.015	0.007	0.005	0.03	10
Resin MIC	0.017	0.019	0.014	0.004	0.05	11
Filter MIC	0.027	0.044	0.040	0.008	0.16	10
Resin Aerochem	0.032	0.042	0.031	0.008	0.13	12
All Samplers	0.020	0.030	0.030	0.004	0.16	43

--- Total PCBs ---

Sampler	Volume Weighted Mean Conc. (ng/L)	Arithmetic Mean (ng/L)	Standard Deviation	-- Range -- Minimum	Maximum	Number
Solvent MIC	2.63	2.83	1.18	1.09	5.35	12
Resin MIC	2.28	2.42	1.52	0.65	5.73	12
Filter MIC	2.66	3.10	1.90	0.90	7.57	13
Resin Aerochem	2.79	3.26	1.86	0.80	7.89	13
All Samplers	2.56	2.91	1.68	0.65	7.89	50

APPENDIX C
CL-PESTICIDE CONCENTRATIONS IN RAIN - 1986

Pesticide concentrations in Precipitation-1986
(ng/L)

-- HCB --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.57	0.44	0.73	0.019	2.73	13
Resin MIC	0.18	0.18	0.35	0.016	1.36	13
Filter MIC	0.12	0.12	0.17	0.007	0.58	11
Resin Aerochem	0.48	0.45	1.05	0.014	3.95	13
all samplers	0.31	0.30	0.70	0.007	3.95	50

-- a-HCH --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	40.8	37.3	57.4	0.10	195.2	10
Resin MIC	44.5	41.6	113.0	0.76	432.4	13
Filter MIC	3.7	3.3	2.7	0.14	8.2	9
Resin Aerochem	3.5	3.5	4.0	0.04	14.1	12
all samplers	28.2	22.4	69.7	0.04	432.4	44

-- b-HCH --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.3	0.3	0.2	0.03	0.7	10
Resin MIC	0.6	0.6	0.5	0.04	1.5	9
Filter MIC	0.6	0.6	0.8	0.08	2.7	8
Resin Aerochem	0.9	1.1	1.4	0.02	3.8	7
all samplers	0.5	0.6	0.9	0.02	3.8	34

--lindane--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	2.8	2.6	1.8	0.02	5.7	10
Resin MIC	3.8	3.4	3.6	0.06	11.4	11
Filter MIC	1.2	1.2	0.9	0.10	2.5	8
Resin Aerochem	1.8	1.5	1.9	0.01	6.4	10
all samplers	2.7	2.2	2.5	0.01	11.4	39

--heptachlor--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.13	0.1	0.2	0.01	0.5	9
Resin MIC	0.58	0.6	1.8	0.004	6.7	12
Filter MIC	0.05	0.1	0.1	0.01	0.2	8
Resin Aerochem	0.95	1.3	3.8	0.01	13.3	11
all samplers	0.40	0.6	2.3	0.004	13.3	40

--heptachlor epoxide--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.3	0.3	0.2	0.02	0.7	10
Resin MIC	0.4	0.4	0.2	0.08	0.8	13
Filter MIC	0.3	0.3	0.2	0.08	0.8	9
Resin Aerochem	0.5	0.5	0.5	0.01	1.5	12
all samplers	0.4	0.4	0.3	0.01	1.5	44

--aldrin--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	4.5	3.6	4.9	0.01	14.1	7
Resin MIC	1.0	1.1	1.5	0.03	5.3	13
Filter MIC	0.5	0.5	0.6	0.07	1.8	6
Resin Aerochem	2.7	2.7	3.6	0.08	11.1	8
all samplers	1.9	1.9	3.2	0.01	14.1	34

--dieldrin--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.7	1.5	1.4	0.12	4.4	11
Resin MIC	2.0	1.7	1.8	0.29	5.8	12
Filter MIC	0.4	0.5	0.4	0.01	1.2	9
Resin Aerochem	1.6	1.8	1.8	0.02	5.4	12
all samplers	1.5	1.4	1.6	0.01	5.8	44

--endrin--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.2	0.2	0.3	0.02	0.8	11
Resin MIC	0.4	0.4	0.8	0.01	3.1	13
Filter MIC	0.2	0.2	0.2	0.04	0.6	9
Resin Aerochem	0.5	0.6	0.9	0.05	3.1	12
all samplers	0.3	0.4	0.7	0.01	3.1	45

-- pp DDE --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.11	0.98	1.4	0.04	3.8	11
Resin MIC	0.90	0.94	2.1	0.07	7.8	12
Filter MIC	0.33	0.33	0.3	0.06	1.1	11
Resin Aerochem	0.92	0.88	1.7	0.09	6.7	13
all samplers	0.81	0.79	1.6	0.04	7.8	47

-- op DDD --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.03	0.03	0.01	0.01	0.05	8
Resin MIC	0.25	0.34	0.59	0.01	1.87	13
Filter MIC	0.11	0.15	0.24	0.01	0.81	9
Resin Aerochem	0.16	0.23	0.49	0.03	1.81	12
all samplers	0.15	0.21	0.45	0.01	1.87	42

-- pp DDD --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.03	0.03	0.02	0.01	0.09	11
Resin MIC	0.07	0.07	0.10	0.00	0.38	12
Filter MIC	0.05	0.08	0.08	0.01	0.27	9
Resin Aerochem	0.07	0.07	0.03	0.03	0.11	12
all samplers	0.05	0.06	0.07	0.01	0.38	44

-- op DDT --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.7	0.6	0.9	0.02	2.6	11
Resin MIC	0.2	0.2	0.5	0.01	1.7	10
Filter MIC	0.1	0.1	0.2	0.01	0.5	8
Resin Aerochem	0.2	0.2	0.2	0.03	0.5	11
all samplers	0.4	0.3	0.6	0.01	2.6	40

-- pp DDT --

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	1.8	1.8	3.0	0.06	10.0	10
Resin MIC	1.1	1.2	2.2	0.12	7.9	11
Filter MIC	0.2	0.2	0.2	0.03	0.6	8
Resin Aerochem	0.6	0.6	1.0	0.08	3.1	11
all samplers	1.1	1.0	2.0	0.03	10.0	40

APPENDIX D
CL-BENZENE CONCENTRATIONS IN RAIN

Data summary: Chlorinated Benzenes in 1986 rain

-- 1,3-DICHLOROBENZENE--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.61	0.90	0.59	0.48	2.60	12
Resin MIC	0.48	0.62	0.53	0.12	2.12	13
Filter MIC	1.26	1.60	0.79	0.12	2.92	12
Resin Aerochem	1.63	2.01	1.03	0.60	3.68	12
all samplers	0.87	1.27	0.94	0.12	3.68	49

-- 1,4-DICHLOROBENZENE--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.91	1.23	1.29	0.12	5.14	13
Resin MIC	0.39	0.55	0.46	0.05	1.64	11
Filter MIC	0.84	1.06	0.77	0.14	2.25	11
Resin Aerochem	1.31	1.57	1.18	0.08	3.41	12
all samplers	0.79	1.12	1.07	0.05	5.14	47

-- 1,2-DICHLOROBENZENE--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.33	0.42	0.40	0.02	1.51	13
Resin MIC	0.59	0.61	0.81	0.01	2.41	13
Filter MIC	1.10	1.99	3.95	0.03	10.81	6
Resin Aerochem	0.97	0.87	0.74	0.03	2.17	12
all samplers	0.69	0.81	1.66	0.01	10.81	44

-- 1,2,4-TRICHLOROBENZENE--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	11.70	14.21	22.66	0.16	80.93	13
Resin MIC	4.05	6.62	12.55	0.28	48.95	13
Filter MIC	10.74	20.28	33.95	0.10	114.74	12
Resin Aerochem	10.67	15.22	16.27	2.19	56.76	12
all samplers	9.07	13.96	23.21	0.10	114.74	50

--HEXACHLOROBENZENE--

sampler	volume weighted mean (ng/L)	arithmetic mean (ng/L)	standard deviation	--range-- min	max	n
Solvent MIC	0.04	0.06	0.10	0.01	0.36	10
Resin MIC	0.04	0.05	0.07	0.01	0.27	12
Filter MIC	0.05	0.06	0.11	0.01	0.41	11
Resin Aerochem	0.04	0.04	0.02	0.02	0.08	12
all samplers	0.04	0.05	0.08	0.01	0.41	45

APPENDIX E
PROPAGATION OF ERROR ANALYSIS

PROPAGATION OF ERROR ANALYSIS

Quantification of a compound's mass in each sample analyzed by the internal standard method involved the equation:

$$M_S = \frac{A_S \times M_{IS} \times CF}{A_{IS} \times RF}$$

where M_S - Mass of compound in sample,

A_S - Chromatographic peak area of sampled compound,

M_{IS} - Mass of internal standard injected into sample,

A_{IS} - Chromatographic peak area of internal standard,

CF - Correction factor for PAH subfraction,

RF - Response factor for compound relative to internal standard from calibration curve.

Inherent in each term is some associated random error. Following the method outlined by Shoemaker et al. (1974) for calculating the propagated uncertainty in the sample mass

$$\sigma M_S = [(\delta M_S/\delta A_S)^2(\sigma A_S)^2 + (\delta M_S/\delta M_{IS})^2(\sigma M_{IS})^2 + (\delta M_S/\delta CF)^2(\sigma CF)^2 + (\delta M_S/\delta A_{IS})^2(\sigma A_{IS})^2 + (\delta M_S/\delta RF)^2(\sigma RF)^2)]^{1/2}$$

where σ - standard deviation.

Performing this calculation and finding σCF negligible, yields:

$$\sigma Ms = \{[\frac{M_S x CF}{A_{IS} x RF}]^2(\sigma A_S)^2 + [\frac{A_S x CF}{RF x A_{IS}}]^2(\sigma M_{IS})^2 +$$

$$[\frac{A_S x CF x M_{IS}}{RF x (A_{IS})^2}]^2(\sigma A_{IS})^2 + [\frac{A_S x CF x M_{IS}}{A_{IS} x (RF)^2}]^2(\sigma RF)^2\}^{1/2}$$

The uncertainty in the sampled compound and internal standard peak area was assumed to equal the relative standard deviation determined from chromatographic reproducibility studies using standard solutions. This relative deviation could then be applied to any subsequent area to estimate the peak uncertainty. The error in the internal standard mass (M_{IS}) was associated with the accuracy of the volume injected into each sample and was estimated to be $\pm$ 2% according to manufacturer's specifications. Thus, σM_{IS} = (IS Conc.)(Inj. Vol.)(0.02). The deviation associated with the response factor was estimated by averaging the response factors determined over the course of the study and calculating the relative standard deviation about this average. It was thought that although this may overestimate the associated error, it would better represent the uncertainty in each response factor than that calculated from each calibration curve. The relative deviation was then applied to each response factor which greatly simplified the propagated error calculations. After multiple calculations ($N \geq 5$) of the uncertainty in the mass, it was found that the relative deviation was nearly constant for any one compound ($\approx \leq \pm$ 0.5%). Therefore, an average relative deviation was applied to all other masses of the same compound.

The uncertainty in the concentration of a compound was also calculated once the mass deviation was determined. Following multiple calculations it was found that the error in the measured volume was negligible and could be omitted. Thus, the uncertainty in the concentration was due entirely to the uncertainty in the quantified mass.

The uncertainty in the volume weighted mean concentration (VWM) was calculated by summing the deviations of each mass and volume and using the equation

$$\sigma VWM = [(1/\sum Vol)^2(\sigma M_S)^2 + [\sum M_S/(\sum Vol)^2]^2(\sigma Vol)^2]^{1/2}$$

Again, after multiple calculations, the deviation about the volume was found to be negligible and the second term in the above equation could be omitted.

Quantification of a compound's mass analyzed by the external standard method involved the equation

$$M_S = \frac{A_S x C_{STD} x CF x V_{VOL}}{A_{STD}}$$

where M_S, A_S, and CF are defined above,

C_{STD} = Concentration of standard solution which is being externally compared to sample,

A_{STD} = Chromatographic peak area of standard solution,

V_{VOL} = Volume of sample in autosampler vial.

Assuming that the uncertainty associated with the subfraction correction factor and the mass of the compound in the standard solution were negligible, the following equation was derived for the uncertainty in the mass.

$$\sigma M_S = \{[\frac{C_{STD} x CF x V_{VOL}}{A_{STD}}]^2 (\sigma A_S)^2 + [\frac{C_{STD} x CF x V_{VOL} x A_S}{(A_{STD})^2}]^2 (\sigma A_{STD})^2 + [\frac{C_{STD} x CF x A_{STD}}{A_{STD}}]^2 (\sigma V_{VOL})^2\}^{1/2}$$

As above, the peak area deviation was determined from reproducibility studies. Thus, $\sigma A_S = \sigma A_{STD}$.

All PAH, PCB, and pesticide uncertainties were calculated using the internal standard method. Since some pesticides were found in both hexane and diethyl ether fractions the reported mass is the sum observed in each fraction and so the uncertainty in the sum is the sum of the uncertainties. Only the chlorinated benzenes were quantified using the external method over the entire sampling period. Since the PCBs and pesticides were both internally and externally quantified during the course of the 1986 rain season, the method that yielded the higher relative mass deviation was applied to all samples. As it turned out the internal method gave higher relative uncertainties. Therefore, the average relative mass deviation determined by the internal method was universally applied to all masses for the uncertainty in the VWM calculation.

APPENDIX F
FIELD NOTES ON PRECIPITATION SAMPLERS - 1986

Summary of 1986 Rain Field Data

sampler name	sampling period from	to	sample code	ave. rainfall (cm)	volume collected (ml)	theoretical volume (ml)	% collection efficiency	Inorganic pH	comments
(1986 Data)	[1]					w/new SA's			
Solvent MIC	12-16	3-15	SM6074	NA	4140	NA	NA		
Solvent MIC	5-8	5-13	SM6133	6.83	8420 +	14070	59.8 +		Overflow
Reservoir MIC	5-8	5-13	RM6133	6.83	13380	13933	96.0		
Resin Aerochem	5-8	5-13	RA6133	6.83	5410	5560	97.3		
Filter MIC	5-8	5-13	FM6133	6.83	13800	14070	98.1		
Inorg. Aerochem	5-8	5-13	IA6133	6.83	4490	4440	101.1	4.47/4.45	
Solvent MIC	5-13	6-12	SM6163	3.86	6960 *	7952	87.5		Cover open when arrived to sample
Reservoir MIC	5-13	6-12	RM6163	3.86	6075 *	7874	77.1		Water in funnel-lost 1L(analyzed 5.08L) & Cover open when arrived to sample
Resin Aerochem	5-13	6-12	RA6163	3.86	2315	3142	73.7		
Filter MIC	5-13	6-12	FM6163	3.86	6580 *	7952	82.8		Water in funnel-Lost 2.6L(analyzed 3.98L)
Inorg. Aerochem	5-13	6-12	IA6163	3.86	1487	2509	59.3	5.62/5.56	
Filter MIC	6-12	6-20	FM6171	0.38	650	783	83.0		Water in funnel-Not enough to analyze
Solvent MIC	6-12	6-23	SM6174	4.57	8460 +	9414	89.9 +		Overflow
Reservoir MIC	6-12	6-23	RM6174	4.57	10090	9323	108.2		
Resin Aerochem	6-12	6-23	RA6174	4.57	2910	3720	78.2		
Filter MIC	6-20	6-23	FM6174	4.19	8560 *	8631	99.2		Water in funnel-lost 2.15L (analyzed 6.41L)
Inorg. Aerochem	6-20	6-23	IA6174	4.57	3100	2971	104.4	5.88/5.94	
Solvent MIC	6-23	7-1	SM6182	1.575	3140	3245	96.8		
Reservoir MIC	6-23	7-1	RM6182	1.575	3140	3213	97.7		
Resin Aerochem	6-23	7-1	RA6182	1.575	NA *	1282	ERR *		No Water in carboy-Vandals?
Filter MIC	6-23	7-1	FM6182	1.575	3000	3245	92.5		
Inorg. Aerochem	6-23	7-1	IA6182	1.575	810	1024	79.1	5.93/5.91	
Solvent MIC	7-1	7-9	SM6190	2.985	6470	6149	105.2		
Reservoir MIC	7-1	7-9	RM6190	2.985	6220	6089	102.1		
Resin Aerochem	7-1	7-9	RA6190	2.985	1970	2430	81.1		
Filter MIC	7-1	7-9	FM6190	2.985	6510	6149	105.9		
Inorg. Aerochem	7-1	7-9	IA6190	2.985	1840	1940	94.8	6.38/6.26/6.26	
Solvent MIC	7-9	7-14	SM6195	2.41	4810	4965	96.9		
Reservoir MIC	7-9	7-14	RM6195	2.41	5050	4916	102.7		
Resin Aerochem	7-9	7-14	RA6195	2.41	490	1962	25.0		
Filter MIC	7-9	7-14	FM6195	2.41	4850 *	4965	97.7 *		Water in funnel-Pumped through resin
Inorg. Aerochem	7-9	7-14	IA6195	2.41	1565	1567	99.9	5.09/5.11	

Summary of 1986 Rain Field Data

sampler name	sampling period from	to	sample code	ave. rainfall (cm)	volume collected (ml)	theoretical volume (ml)	% collection efficiency	Inorganic pH	comments
Solvent MIC	7-14	7-22	SM6203	2.79	6250	5747	108.7 *		two intense rain
Reservoir MIC	7-14	7-22	RM6203	2.79	5930	5692	104.2 *		events, including
Resin Aerochem	7-14	7-22	RA6203	2.79	2350	2271	103.5 *		one tornado approx
Filter MIC	7-14	7-22	FM6203	2.79	5690	5747	99.0 *		ten miles south
Inorg. Aerochem	7-14	7-22	IA6203	2.79	1400	1814	77.2	5.53/5.53	
Solvent MIC	7-22	7-31	SM6212	4.305	8130	8868	91.7		*
Reservoir MIC	7-22	7-31	RM6212	4.305	7090 *	8787	80.7 *		Cover open when arrived to sample
Resin Aerochem	7-22	7-31	RA6212	4.305	3750 *	3504	107.0 *		Water in reservoir drained through resin
Filter MIC	7-22	7-31	FM6212	4.305	8530 *	8868	96.2 *		Water in funnel pumped through resin
Inorg. Aerochem	7-22	7-31	IA6212	4.305	2690	2798	96.1	6.69/6.68	
Solvent MIC	7-31	8-11	SM6223	4.064	8220	8372	98.2		
Reservoir MIC	7-31	8-11	RM6223	4.064	8020	8291	96.7		
Resin Aerochem	7-31	8-11	RA6223	4.064	2530 *	3308	76.5 *		Water in reservoir drained through resin
Filter MIC	7-31	8-11	FM6223	4.064	7890 *	8372	94.2 *		Water in funnel pumped through resin
Inorg. Aerochem	7-31	8-11	IA6223	4.064	2710	2642	102.6	6.40/6.39	
Solvent MIC	8-11	8-25	SM6237	3.327	4930	6854	71.9		
Reservoir MIC	8-11	8-25	RM6237	3.327	5750 *	6787	84.7 *		Water in reservoir pumped through resin
Resin Aerochem	8-11	8-25	RA6237	3.327	2920	2708	107.8		
Filter MIC	8-11	8-25	FM6237	3.327	250 *	6854	3.6 *		Fuse Blown
Inorg. Aerochem	8-11	8-25	IA6237	3.327	2100	2163	97.1	4.50/4.47	
Solvent MIC	8-25	9-12	SM6255	4.267	8250 *	8790	93.9 *		Overflow
Reservoir MIC	8-25	9-12	RM6255	4.267	9410	8705	108.1		
Resin Aerochem	8-25	9-12	RA6255	4.267	3530	3473	101.6		
Filter MIC	8-25	9-12	FM6255	4.267	8880 *	8790	101.0 *		Water in funnel-pumped through resin
Inorg. Aerochem	8-25	9-12	IA6255	4.267	2620	2774	94.5	4.82/4.80	
Solvent MIC	9-12	9-22	SM6265	8.966	15040 *	18470	81.4 *		Overflow
Reservoir MIC	9-12	9-22	RM6265	8.966	16710 *	18291	91.4 *		Water in reservoir-drained through resin
Resin Aerochem	9-12	9-22	RA6265	8.966	8100 *	7298	111.0 *		Water in reservoir-pumped through resin
Filter MIC	9-12	9-22	FM6265	8.966	16650 *	18470	90.1 *		Water in funnel/Cover Open/Fuse Blown
Inorg. Aerochem	9-12	9-22	IA6265	8.966	5810	5828	99.7	4.96/4.94	
Solvent MIC	9-22	10-13	SM6286	3.975	7620	8189	93.1		
Reservoir MIC	9-22	10-13	RM6286	3.975	3910 *	8109	48.2 *		Water in reservoir-Pumped through resin
Resin Aerochem	9-22	10-13	RA6286	3.975	3280	3236	101.4		
Filter MIC	9-22	10-13	FM6286	3.975	8350 *	8189	102.0 *		Water in reservoir-pumped/Cover open/Shut down
Inorg. Aerochem	9-22	10-13	IA6286	3.975		2584			
Solvent MIC	10-13	11-14	SM6318	1.664	3030	3428	88.4		Rain/Snow
Reservoir MIC									Removed From Field/Extracted Reservoir
Resin Aerochem									Removed From Field/Extracted Reservoir
Filter MIC									Removed From Field/Extracted Reservoir
Inorg. Aerochem	9-22	11-14	IA6318	5.639	3160	3665	86.2	5.40/5.37	Removed from Field
Solvent MIC	11-14	12-4	SM6338	?	2000 *	?	? *		No Rain/Snow Gauge